NBS TECHNICAL NOTE 546

Analytical Mass Spectrometry Section:

Summary of Activities July 1969 to June 1970

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Edited by William R. Shields

Analytical Mass Spectrometry Section
Analytical Chemistry Division
Institute for Materials Research
National Bureau of Standards
Washington, D.C.   20234

The Analytical Chemistry Division was established as a
separate division at the National Bureau of Standards on
September 1, 1963, and became part of the Institute for
Materials Research in the February 1, 1964, reorganization.
It consists at present of nine sections and about 100 tech-
nical personnel encompassing some 60 different analytical
competences from activation analysis and atomic absorption to
vacuum fusion and x-ray spectroscopy. These competences, and
in turn the sections which they comprise, are charged with
research at the forefront of analysis as well as awareness of
the practical sample, be it standard reference material or
service analysis. In addition it is their responsibility to
inform others of their efforts.

Formal publication in scientific periodicals is a highly
important output of our laboratories. In addition, however,
it has been our experience that informal, annual summaries of
progress describing efforts of the past year can be very valu-
able in disseminating information about our programs. A word
is perhaps in order about the philosophy of these yearly
progress reports. In any research program a large amount of
information is obtained and techniques developed which never
find their way into the literature. This includes the
"negative results" which are so disappointing and unspectacu-
lar but which can often save others considerable work. Of
importance also are the numerous small items which are often
explored in a few days and which are not important enough to
warrant publication--yet can be of great interest and use to
specialists in a given area. Finally there are the experimen-
tal techniques and procedures, the designs and modifications
of equipment, etc., which often require months to perfect and
yet all too often must be covered in only a line or two of a
journal article.

Thus our progress reports endeavor to present this infor-
mation which we have struggled to obtain and which we feel
might be of some help to others. Certain areas which it
appears will not be treated fully in regular publications are
considered in some detail here. Other results which are
being written up for publication in the journal literature
are covered in a much more abbreviated form.

At the National Bureau of Standards publications such as
these fit logically into the category of a Technical Note.
In 1970 we plan to issue these summaries for all of our
sections. The following is the fifth annual report on pro-
gress of the Analytical Mass Spectrometry Section.

W. Wayne Meinke, Chief
Analytical Chemistry Division

PREFACE

The primary function of the Analytical Mass Spectrometry Section is to establish high accuracy absolute abundance ratio standards. The atomic weight associated with the absolute abundance ratio is of course the real product if the element shows no variation in nature.

As the generation of each new standard seems to take more and more effort we have looked around for ways to keep the rest of the staff busy during the development period. The most logical second use of the abundance ratio measurement is assay by isotope dilution, and for the past several years we have made a major effort to develop this competence and apply it to the characterization of various SRMs. As you read this past years summary of activities you will see that indeed we have applied this tool, and have been called on to determine concentrations that range over seven orders of magnitude (from nickel at 10% to thallium at 8 ppb) and have been able to maintain a rather good level of precision and accuracy even at the lower concentration.

The transfer of the spark source group to the section is a logical extension of this work and permits even lower determinations of concentration by isotope dilution, and at the same time increases the number of elements that the section can detect and analyze.

Even with all the busy work the staff has still managed to add several new standards to its portfolio. The two new uranium SRMs are end point standards and are the culmination of many years of experience before ratios as large as they contain could be certified.

In order to specify adequately some of the procedures and equipment changes it has been necessary occasionally to identify commercial materials and equipment in this report. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

William R. Shields, Chief
Analytical Mass Spectrometry Section

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

x

ANALYTICAL MASS SPECTROMETRY SECTION: SUMMARY OF ACTIVITIES
JULY 1969 TO JUNE 1970

Edited by William R. Shields

This report describes the advances in instrumentation and the research activities of the Analytical Mass Spectrometry Section during the period July 1969 to June 1970.

Advances in instrumentation include the construction of a computer controlled mass spectrometer with appropriate interconnecting components, power supplies with greatly increased stability and the utilization of a magnetic field control.

Elements studied during this period include: B, Cu, Ag, Pb, Tl, U, Pu, K, Rb, Ni and Mo. Chemical procedures are given for Cu, Ag, Pg, Tl, U, K, Rb, Ni and Mo. Mass spectrometric procedures are given for Pb, Tl, U, K, Ni and Mo. Chemical procedures for the intercomparison of redox standards are also given.

Key words: instrumentation; isotopic analysis; mass spectrometry; procedures.

1. INSTRUMENTATION

A. Multistage Instruments

During the past year several changes and additions have been made in the electronic components for the multistage instrument. These changes were in two general areas; to improve magnet control and stability and to increase the switching speed of the accelerating potential switching system. The changes are described in detail below.

1. Magnet Control and Stabilization

Absolute magnet field control with a high degree of stabilization has long been sought as an adjunct to precision analytical mass spectrometry. Utilizing the newly released Varian Model FR-40 Gaussmeter-Controller an absolute magnetic field control system has been designed and installed in this laboratory.

Modification of the magnet power supply normally used was necessary to provide a compatible input and to achieve a high loop gain providing tight control. A schematic diagram of the suitably modified magnet power supply is shown in figure 1. An operational amplifier was used to provide a dc gain of 100 with lag-lead compensation to permit stable system operation. Settling time for a change of 100 Gauss is less than 3 seconds in controlled operation. The final control achieved with this system is a minimum of 1 part in 800,000 and is typically greater than 1 part in one million. The results at this point have been most gratifying in that no magnet drift or instabilities have been detected in the use of the controller during mass spectrometer operation.

It should be noted that the modifications made on the standard magnet power supply include several changes that improve the normal or non-field-controlled operation. These changes may be easily incorporated in an existing system even though no controller is to be used and these are separately identified in figure 1.

The feedback voltage is reduced to 0-9 volts by replacing the current sense resistor string between the cathodes of the 6146 to ground. A voltage reference diode (1N938A) is used to provide a very stable voltage source to the 25 turn control potentiometer. This diode is mounted in a heat shield located at the front right of the chassis, the most thermally stable location on the supply. The ground from the diode as well as that from the control pot and the current sense resistor string must all be attached to the same specific point to avoid ground loop and noise. The last two modifications are the additions of a 0.1 mfd capacitor to the grid of the last 12AX7 to prevent instability and the exchange of the input 12AY7 for a 12AX7 which increases the open loop or excess gain.

2
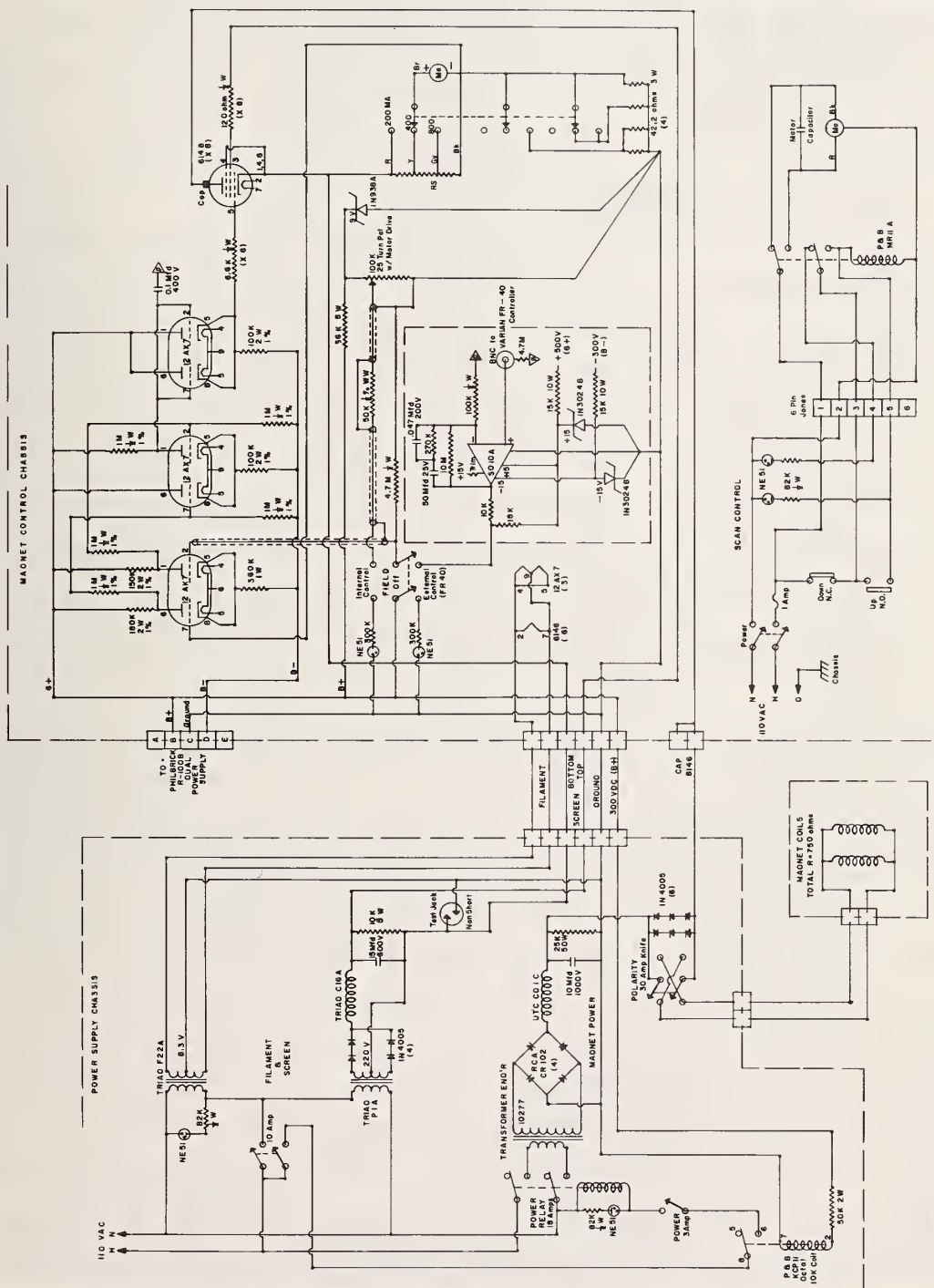
Figure 1. Magnet Control Circuit.

3

The modifications as described improve the current stability by at least a factor of three and have substantially increased the useful operating time between failures.

B. High Voltage Switching System

A newly designed high voltage or acceleration potential switching system has been installed that allows much higher speed of switching as well as containing provision for manual operation or operation under complete computer control including voltage selection, timing and peak centering.

1. Design and Construction

A different concept in voltage scanning has been employed to eliminate the unduly long settling time of the previously used accelerating voltage control system. In this new configuration, a second power supply is used to provide a voltage offset of up to 1000 volts added to the accelerating voltage (figure 2). This second power supply is a fast slewing type (50 v/μs) which behaves as an ultra stable very high voltage operational amplifier and is operated in a resistance programmed mode. The resistances used to set the system accelerating voltage are series switched by the voltage scan control unit.

The voltage scan control unit contains fifteen precision ten turn potentiometers and relay switching to permit automatic or manual selection of any of fifteen mass locations within the 1000 volt range of the power supply. Indication and manual selection are done with a combined light and push button switch associated with each voltage setting potentiometer. Each voltage setting resistor covers a range of up to 100 volts. The voltage offset supplied is the voltage setting selected plus the sum of all the voltage settings of each higher number. A sixteenth potentiometer, with an effective 100 turns of control, is situated at the top end of the resistor string and covers the full 1000 volts of range. This control is driven by a variable speed stepping motor which can also be manually

4

Figure 2. Relay Board and High Voltage Reference.

5

or remotely controlled. The remote feature enables the computer to operate in an automatic peak centering mode.

Under computer control, the unit is completely slaved to a set of nine output commands or bits issued from an auxilliary relay driver attached to the computer (figure 2). The first eight bits specify manual (0) through voltage position 7 and voltage positions 8 through 15. The ninth bit selects the upper or lower group. When no bits are active, the unit operates in the manual mode. The unit is self contained and need not be connected to any control unit for manual operation.

Implementation of the instrument logic is done entirely with reed relays (figure 2). Three of the relays are DPDT, and sixteen relays have one double throw reed switch and one high voltage single throw switch. In computer or programmer controlled operation, a series of diodes form an OR gate to sense the presence of a control signal on the input lines, energizing relays B & C. In this configuration, no relay logic is performed, and each individual voltage selecting relay is actuated solely by current sinking of the relay drivers with relay D selecting the upper or lower voltage group as desired (figure 2). When no control bits are present or when the programming device is disconnected, relays B & C are deenergized, and the unit is configured for manual operation. In this form of operation, each relay becomes a latching circuit where the lowest number relay energized opens its N.C. contact which denies the power return path to all higher numbered relays. This circuit excludes the possibility of more than one voltage relay being closed at any one time. Transfer of control from one relay to the next is accomplished by activating one of the other push button switches. When a higher number push button is depressed, the negative current path to the selected relay through the N.C. contacts of each higher number push button switch is maintained while this path is removed from the lower numbered relay still in control.

6

Negative current is still supplied to the lower numbered relay through the N.C. contacts of relay A. When the push button switch is fully depressed, it supplies positive current to the selected relay via the N.O. contacts, placing the coil of relay A in series with the coil of the selected relay. When relay A energizes, the negative current supplied through its N.C. contacts is removed, dropping out the lower numbered relay and transferring control to the relay selected by the push button. The transfer of control from a higher to a lower numbered relay is done when the lower push button is depressed, activating its associated relay which immediately assumes control when its N.C. contacts open and removes the current return path from the coil of the higher numbered relay. In each of the cases described above, the newly selected relay circuits are established before control is released from the previously selected circuit, ensuring a smooth and direct transition at the output of the high voltage power supply. A second set of contacts on relay A is available to be used as a priority interrupt flag to halt a program and resume manual control when a push button is depressed.

The power supply and stepping motor control circuits are shown in figure 3. Up and down drive signals to the stepping motor are provided either by the front panel switch or by energizing one of the two relays. Another mode of operation permitting single pulses to step the motor is included in the circuit. By using the pulse forming capacitor, resistor, diode network connected to each of the two control lines, a timed pulse (50-200 μs) issued by the relay driver unit is of insufficient duration to pull in the relay but will couple to the stepping motor control circuit as a single pulse. This arrangement allows a discrete number of pulses to be generated by the computer regardless of the setting of the speed control.

Figure 3. Power Supply and Scan Control.

8

The power dropout relay disconnects the ground return line from the remote relay driver unit if that unit is turned off. This is required to allow the internal ground to float, permitting normal manual operation. Otherwise, when its negative power supply goes to zero volts output, current return paths are supplied through the kick-back diodes located in the driver unit.

2. Vibrating Reed Electrometer Remote Ranging

A remote ranging vibrating reed electrometer (VRE) was coupled to the computer output relay driver unit through a reed relay interface (figure 4). This was done since the remote ranging feature of the VRE was not readily adaptable to the customarily used relay driver circuits. The interface circuit is no more than a set of nine relay repeaters between the two circuits. One extra relay circuit was added to permit remote operation of the input shorted switch, allowing for a computer operated current integrate mode for low level measurement. A two transistor circuit was added to override the computer control of the remote ranging by setting the local/remote switch in the local position.

3. Performance

The characteristics of the 1000 volt fast slewing supply are such that switching between voltages corresponding to any two mass positions may be accomplished completely within 2.5 milliseconds.

In addition the voltage supply system shows excellent short term stability and reproducibility as shown in Table 1. This typical data demonstrates that a short term stability of about 60 millivolts may be expected while the setting at any one voltage position may be reproduced to within 20-30 millivolts. Since the flat position of a peak is nominally 4.5 volts wide with this instrument no difficulty has been experienced with peak positioning.

9
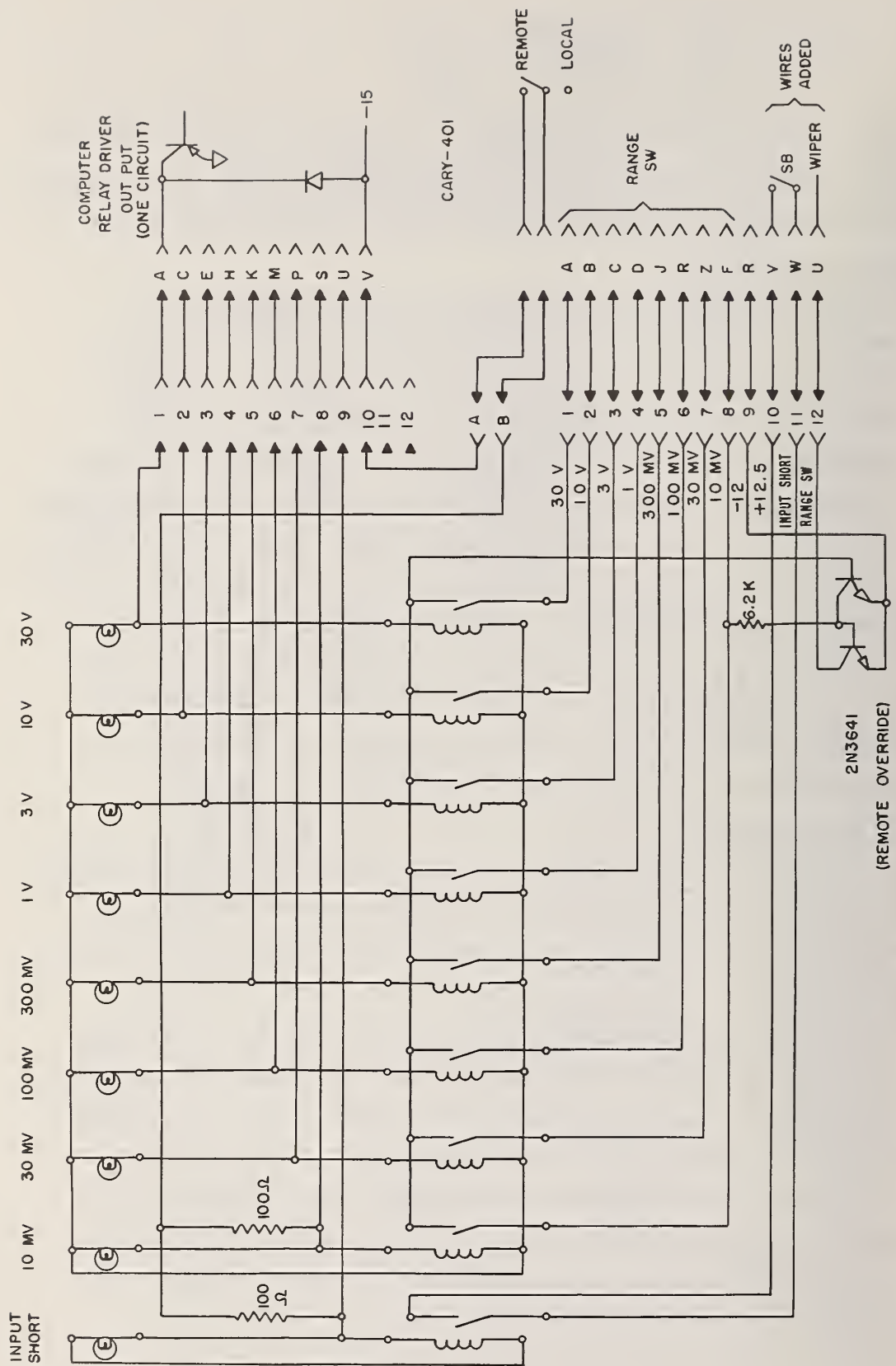
Figure 4. Electrometer Programmable—Range Control.

10

Table 1. Measurement of voltage switching panel stability.

a. Voltage readings taken at 1 minute intervals at 1 mass position after 10 minute warm–up.

Time (minutes)	Voltage (volts)	Time (minutes)	Voltage (volts)
1.	329.56	6.	329.54
2.	329.52	7.	329.58
3.	329.54	8.	328.53
4.	329.55	9.	329.58
5.	329.52	10.	329.58

b. Voltage readings taken after switching to alternate mass position. Readings taken at approximately 15 second intervals and at approximately 0.1 seconds after switching.

Position 12	Position 5
330.74 volts	475.18 volts
330.75	475.18
330.74	475.17
330.74	475.17
330.73	475.17
330.74	475.17
330.72	475.17

C. Mass Spectrometer, 12 inch, 90°

As a part of a cooperative project with personnel of the Geological Sciences Division, Lunar Sciences Institute, Manned Spacecraft Center, N.A.S.A., a new 90° automatic mass spectrometer has been completed and tested at NBS and put into operation at M.S.C. A description of the instrument and its various operating systems is given below:

1. General Description

The instrument is a 90°, 12 inch radius extended flight path spectrometer with the magnet arranged so that the flight tube is mounted in a horizontal plane. It is equipped with an air operated beam valve [1], a thin lens "Z" focussing

11

source [2] and a collector with faraday cage, transmission
and electron suppressing grids [2]. The collector housing is
arranged so that an electron multiplier may be mounted in
place of the faraday cage if desired, although a multiplier
is not normally a part of the collector system.

2. Electrical Components

The spectrometer contains a magnet field measuring-control
system as described above for the multi-stage instrument.
Although the field cannot be changed automatically as currently
arranged, the addition of this feature to the field controlled
system would be relatively simple.

This instrument is also provided with a high voltage or
acceleration potential switching system as described above.

The collector grid output is measured with a vibrating
reed electrometer (VRE) and the faraday cage output with a
second VRE. The cage electrometer contains provisions for
automatic, programmable range selection as well as an auxiliary
-10 V(FS) output. This 10 V output is connected to a -10
V(FS), 12 bit analog to digital converter which is a part of
a small digital computer.

3. Computer System

An integral part of the instrument is a small high speed
digital computer which handles the functions of peak selection
(via high voltage switching), electrometer range selection,
timing and data collection, manipulation, storage and display.
The system contains a 12 bit digital computer with 8K memory,
programmable crystal clock and 2 small magnetic tape drives
with controller. Also present are an output relay driver
control with 36 relay drivers, a six (decimal) bit nixie
display and the high speed A-D converter previously mentioned.

4. Programming

A versatile, two isotope program was written for this
system by Mr. Charles Krpec, Systems Analyst, Computational
and Analysis Branch, Manned Spacecraft Center.

12

The program was written in the conversational language Focal with assembly language sub-routines to control the A-D converter and relay drives. During programmed operation the computer selects relays related to mass positions, chooses the proper electrometer relay, inserts a delay time for amplifier settling, takes data at the rate of 150 12 bit conversions per second and scales, prints and displays the average converter reading, ratio and average ratio.

Delay times, number of converts, number of sets of converts and number of ratios recorded are easily set by the operator and may be changed at will. A copy of this program will be supplied upon request.

5. Performance

A set of 10 analyses were made by Dr. Norman Hubbard of the Manned Spacecraft Center on uranium standards where the $^{235}U/^{238}U$ ratio varied from 1:20 to 20:1. These analyses were performed using the triple filament technique [3] and magnet flipping with data recorded on an expanded scale strip chart recorder [3]. The results of this test showed a single correction factor for filament bias (theoretical value/experimental value) of 0.99598±0.00124 (95% C.L. for a single analysis).

The same test was performed with voltage switching and with the data collected with the computer. The bias factor determined was 0.99196±0.00038. This defines a voltage switching correction factor of 0.0040 or 0.134%/mass unit.

A single set of 10 analyses of the B & A shelf standard strontium gave an average normalized value of $^{87}Sr/^{86}Sr$ = 0.7079±0.0004/analysis.

13

2. ISOTOPIC STANDARDS

A. Uranium Isotopic Standards

1. U-0002 and U-970 Proposed Uranium Isotopic Standards

Two new uranium isotopic standards have been analyzed for certification. One, U-0002, is a depleted sample of U_3O_8 having approximately 0.02 atom percent ^{235}U and the other, U-970, is an enriched sample of U_3O_8 having approximately 97 atom percent ^{235}U. The minor isotopes in both samples determined by isotope dilution mass spectrometry with a "U-233" separated isotope. In addition known synthetic mixtures of "U-235" and "U-238" separated isotopes were prepared to approximately equal the ^{235}U and ^{238}U composition of the U-970. These mixtures were prepared to determine the mass spectrometer bias at this composition.

Samples of the two prepared standards were ignited to give a reproducible oxide [ref. 1, p. 37]. Two 0.1 g samples of the "U-233" separated isotope were ignited by the same procedure and after dissolving in nitric acid (1+1), they were diluted to approximately 100 g with water. Weighed aliquots, using plastic syringes and platinum needles, were added to the dissolved U-970 samples to approximately equal the ^{234}U or the ^{238}U content in the U-970 sample. Weighed aliquots of the "U-233" solutions were diluted by weight to produce a solution containing approximately 40 µg U per gram of solution. Weighed aliquots of the dilute "U-233" solutions were added to the U-0002 samples to approximately equal the ^{235}U or ten times the ^{234}U content of the U-0002 sample.

The ^{235}U and ^{238}U mixtures were prepared in a similar manner by adding weighed aliquots of "U-238" solutions containing approximately 1.4 mg U/g to dissolved "U-235" samples.

The first results on the "U-233" spiked samples indicated approximately 0.4 percent difference in samples spiked with one "U-233" solution compared to samples spiked with the second "U-233" solution. In order to check the ^{233}U concentration

14

in the two spike solutions, weighed aliquots of both "U-233"
samples were spiked with two "U-235" separated isotope solu-
tions. The agreement between this check "spike calibration"
and the calculated concentration of ^{233}U from the weight of
"U-233" separated isotope was within 0.05 percent. The second
"U-233" solution disagreed by 0.51 percent. The ^{233}U concen-
tration was lower by 0.51 percent indicating an impure sample,
loss of sample or incorrect recording of weights. When the
corrected value is used for the "U-233" solution the results
agree within experimental error.

   2. <u>Mass Spectrometry (U-0002 and U-970)</u>

   SRM U-0002 and SRM U-970 are the end points in the series
of uranium isotopic standard reference materials. They also
represent to some degree extremes in ion current measurements
and require some additional precautions that were not critical
for some of the other uranium SRMs. The general procedure for
determination of the isotopic composition of a uranium sample
is a point calibration of the $^{235}U/^{238}U$ ratio and ^{233}U isotope
dilution analysis to determine ^{234}U and ^{236}U.

   A 12 inch radius of curvature 68° analyzer tube mass
spectrometer was used to determine the isotopic composition
of U-970 and only the ^{235}U composition of U-0002. The more
important characteristics of this instrument have been dis-
cussed in previous reports [2,3]. The NBS standard collector
[2] was used as the ion current detector and the output of the
vibrating reed was used to drive an expanded scale recorder.

   The ^{234}U composition of U-0002 was determined by pulse
counting on the multistage mass spectrometer. Characteristics
of the multistage instrument have also been previously
discussed [1,4].

   The sample mounting procedure, sample degassing and a
general analytical pattern are described below. Specific
details of low-temperature and high-temperature uranium anal-
yses for instruments without "Z" optics are discussed in
Technical Note 277 [3]. The precautions taken to measure

large ion current ratios are given in last year's report [4]. Unless stated to the contrary the sample size per analysis was always 200 µg for the 12 inch single stage instrument.

3. U-0002; Determination of ^{235}U by Isotope Dilution

A high temperature analytical procedure for the "Z" lens source was used and the total ion current for an analysis was $4-5\times10^{-10}$ A. Ten peak sets of data were taken for each analysis at a constant ion accelerating voltage (10 KV) and the ^{235}U and ^{233}U were scanned by changing the magnetic field with the electromechanical scan control.

The standard procedure of a 15 minute degassing of the sample and a minimum waiting period of 1/2 hour before starting the analysis was not used for U-0002. Under these conditions the estimated collector vacuum was too high and scattered particles rendered baselines at the ^{235}U and ^{233}U mass positions indeterminate. With respect to the ^{238}U ion current of $4-5\times10^{-10}$ A the interference was less than a part in one hundred thousand, but was approximately 2-5 percent of the ^{233}U and ^{235}U peak heights.

The normal continuous baseline curve was obtained when the collector pressure was estimated to be in the low 10^{-7} torr region. To achieve this pressure it was necessary to modify and condense the normal pumping time for a uranium analysis as follows: Allow 5 minutes of source pumping by the mercury diffusion pump; open the tube beam valve and allow an additional 10 minutes for pumping; add liquid nitrogen to the source coldfinger and start the degassing procedure.

Immediately after completing the degassing step the ion accelerating voltage was adjusted to 10 KV and the high temperature analysis was started. After a combined total of 30 minutes of heating, the filaments were turned off, the tube beam valve was closed and the source coldfinger was warmed to room temperature. After a 5 minute waiting period, liquid nitrogen was added to the source coldfinger and the analysis restarted. A 4×10^{-10} A uranium ion current was obtained in

16

the prescribed manner for a high-temperature analysis during the next 20 minutes. Therefore, between 50 and 60 minutes were necessary to arrive at a point where data could be taken with an estimated collector pressure of $1-4\times10^{-7}$ torr. Extensive pumping either before or after degassing, even with the beam valve open, was not utilized because the collector vacuum would become too high before the analysis could be completed. It was necessary to complete the analysis within 2 hours after the start of pumping on the sample or run the risk of high vacuums with detectable interference at the baselines.

Under conditions of the standard procedure of degassing, minimum 1/2 hour waiting period and then analysis of a sample, no organic background is detected at a 10^{-15} A ion current sensitivity. A suspected organic background was occassionally detected when the waiting period between degassing and analysis was omitted. A 5-10 minute waiting period was found to be effective in reducing the suspected organic background below the detection limit of the mass spectrometer.

The correction for mass discrimination was determined by analyzing SRM U-500 on a cleaned source and under the same conditions as the spiked samples. The isotopic composition of ^{235}U was calculated by taking the product of the corrected $^{235}U/^{233}U$ ratio and the amount of ^{233}U (atom percent) added to the sample. Contribution of ^{235}U from the spike was always below the detection limit of the instrument and no correction was made.

4. U-970; Point Calibration of $^{235}U/^{238}U$ Ratio

Point calibration was mandatory for accurate measurement of the large $^{235}U/^{238}U$ ratio because of significant R-C response of the measuring circuit when switching from a 10^{-11} A ion current to a 10^{-13} A ion current. To minimize any systematic error contribution from R-C response, all peak top observations for the ^{238}U ion current were extended to 60 seconds and only the last 30 seconds were used as data for peak height determination. An upper limit of 5×10^{-11} A was used for ^{235}U ion

17

currents to avoid operation at intensities where non-linear response of the 10^{11} ohm input resistor was a source of systematic bias.

To accomplish the point calibration, U-970 and four synthetic mixtures with known ^{235}U and ^{238}U composition of approximately the same ratio as U-970 were analyzed in an alternate pattern until duplicate analyses of each calibration sample was obtained. A correction factor for mass discrimination was determined from the ratio of the theoretical $^{235}U/^{238}U$ to the observed $^{235}U/^{238}U$ of the calibration samples and the absolute $^{235}U/^{238}U$ ratio of U-970 was calculated.

5.   Determination of ^{234}U in U-0002 by Pulse Counting

The same set of U-0002 samples, which were spiked with the "U-233" solution and used for determination of the ^{235}U content, also presented an opportunity to determine the ^{234}U content, which was known to be ⌁2 ppm. To provide a statistically useable ^{234}U signal of ⌁100 counts per second, an equivalent ^{238}U signal of approximately 50 million counts was required. The single V filament technique used for the 0.02 ppm Trace Elements in Glass series (see section 3-B) proved to be inadequate in terms of total signal intensity available. Therefore, a fourfold modification of the conventional triple filament technique was used:

(1)   Ionizing and sample filaments were degassed at ⌁2050 °C for one hour.

(2)   One-half the usual amount of uranium was used; i.e., approximately 50 μg per sample filament.

(3)   A 30 minute degassing period was used prior to analysis, with the ionizing filament set at 2150 °C and the sample filament currents set at 1.75 A.

(4)   An ionizing filament temperature of 1900 °C was used during analysis to eliminate the contribution of organic ions to the uranium spectrum.

A final ^{238}U signal of ~1.6 V gave the requisite 100 cps ^{234}U signal.

A scan of the mass region from m/e 237 through 233 during an analysis of U-0002 spiked with "U-233" solution showed there was no discernible organic or other contribution to mass position 236; nor in a scan of unspiked U-0002 was there any evidence of a contribution to the 236 or 233 mass positions. Therefore, the only correction required for any contribution to the various mass positions above the normal background was for the scatter due to the tail of the large 238 beam. To determine the magnitude of the correction, a count was taken, immediately prior to analysis, for 100 seconds at the half-mass positions on either side of each integral mass position of interest. An average of the two half-mass counting results then represented an approximate scatter correction for the corresponding integral mass position. Since the scatter correction for the ^{234}U amounted to ~5 percent of the total count, the accuracy of the analysis was limited largely by the inability to accurately correct for scatter.

A mass discrimination correction was applied by also measuring the $^{233}U/^{235}U$ ratio and comparing with the corresponding ratio as determined by the conventional triple filament technique.

6. ^{233}U Isotope Dilution of U-970

Two groups of 3 spiked U-970 samples were provided for analysis. The three-fold purpose of the equal atom ^{238}U group was to evaluate the potential of determining ^{238}U by isotope dilution; to provide a spike within several orders of magnitude of the ^{236}U abundance; to obtain data on a $^{234}U/^{233}U$ measurement of some ratio other than 1.

A low temperature analytical procedure for the "Z" lens ion source was used. The ^{234}U, ^{236}U and ^{238}U were measured with respect to ^{233}U with total ion currents between $5-7 \times 10^{-11}$ A. Each set of equal atom samples was analyzed as a group. For the equal atom ^{234}U solutions results were

19

obtained for each analysis in the following sequence and number of ratios: 235/238, (5); 234/233 and 236/233 (4 each); 238/233, (5); 236/233 and 234/233 (4 each); 235/238, (5). For equal atom ^{238}U solutions results were obtained for each ratio in the following sequence and number of ratios: 235/238, (5); 238/233, (5); 234/233 and 236/233, (5 each); 238/233, (5); 235/238, (5). At all times the 235/238 and the 238/233 ratios were measured by alternately monitoring peak tops for 30 seconds. The 234/233 and the 236/233 ratios were measured by normal mass scanning (magnet) but a quick-scan step ($\sim$2 seconds) was used to scan over the ^{235}U peak.

The correction for mass discrimination was determined by analyzing SRM U-500 on a cleaned source and under the same conditions as the spiked samples. Compositions of ^{234}U, ^{236}U and ^{238}U were calculated by taking the product of the abundance ratio corrected for filament bias and the amount of ^{233}U (atom percent) added to the sample, and where applicable, subtracting the contribution of these isotopes made by the ^{233}U spike. The contribution from the spike was determined by dividing the micromoles of the isotope in the spike solution by the micromoles of uranium in the U-970 solution and multiplying by 100.

The ^{238}U value calculated from the point calibration value of the ^{235}U/^{238}U ratio and the isotope dilution values for ^{234}U and ^{236}U were considered to be best values and were used to obtain the ^{235}U by difference.

The results of the analyses of U-0002 and U-970 are given in Tables 2, 3, 4 and 5.

Table 2. Determination of correction factor for calibration of $^{235}U/^{238}U$ ratio of SRM U–970, Uranium Isotopic Standard.

Calibration sample no.	Calculated $^{235}U/^{238}U$	Observed $^{235}U/^{238}U$		Correction factor
17–86	193.785	194.7911		0.994834
		194.8260		0.994656
			Average	0.99474
17–92	190.956	191.9724		0.994705
		191.8785		0.995192
			Average	0.99494
17–93	197.106	198.3268		0.993844
		198.1157		0.994903
			Average	0.99437
17–94	191.316	192.3996		0.994367
		192.2831		0.994970
			Average	0.99467

Mean Correction Factor = 0.99468

Table 3. Determination of the $^{235}U/^{238}U$ ratio of SRM U–970, Uranium Isotopic Standard.

Run no	Observed $^{235}U/^{238}U$	Corrected $^{235}U/^{238}U$
3–2209	187.6788	186.680
3–2211	187.7381	186.739
3–2214	187.7164	186.718
3–2216	187.6868	186.688
3–2218	187.8737	186.874
3–2220	187.9418	186.942
3–2223	187.7633	186.764
3–2225	187.8467	186.847
Average	187.780	186.782
s.d.		± 0.095

Table 4. Isotopic composition of SRM U–970, Uranium Isotopic Standard as determined by "U–233" isotope dilution.

Sample no.	^{234}U atom %	^{236}U atom %	^{238}U atom %
17–76[a]	1.6655	0.1493	0.5233
17–78[a]	1.6660	0.1489	0.5225
17–84[a]	1.6655	0.1492	0.5233
17–77[b]	1.6656	0.1490	0.5231
17–83[b]	1.6642	0.1492	0.5228
17–85[b]	1.6649	0.1491	0.5232
Average	1.6653	0.1491	0.5230
s.d.	± 0.0006	± 0.0001	± 0.0003

[a] "U–233" solution 17–95 used.

[b] "U–233" solution 19–96 used.

Table 5. Isotopic composition of SRM U–0002, Uranium Isotopic Standard.

Sample no.	^{234}U atom %	^{235}U atom %
17–68[a]	0.000164	– – – –
17–69[a]	0.000157	0.017547
17–73[a]	– – – –	0.017543
17–70[b]	0.000162	– – – –
17–71[b]	0.000158	0.017554
17–72[b]	0.000158	0.017551
Average	0.000160	0.017549
s.d.	± 0.000003	± 0.000005

[a] "U–233" solution 17–95 used for isotope dilution.

[b] "U–233" solution 17–96 used for isotope dilution.

B.   Stoichiometry of Uranium Oxide

This investigation [ref. 4, p. 19] was undertaken in the hopes of finding an easily reproducible ignition procedure that would give a stoichiometric U_3O_8 compound. Only under very carefully controlled conditions could this be approached. Changes in temperature, pressure, cooling rate or oxygen content of the ignition gas result in changes in the stoichiometry of the uranium oxide. Following the same procedure used last year, samples of 1 g of SRM 950a, Uranium Oxide, (U_3O_8), were ignited in a tube furnace [1]. The samples were placed in platinum boats and weighed on a microbalance while sealed in a small desiccator.

Table 6 shows the results, including some reported last year, of a series of ignitions at increasing temperatures with varying cooling rates. Three cooling rates were used. The samples were cooled by taking 10-15 minutes to move the furnace back from the samples (slow cooling), by quickly moving the furnace back from the area of the tube containing the samples (normal cooling) or by quickly pulling the sample boat into an iced portion of the quartz tube (fast cooling). To obtain a stoichiometric oxide would require a loss on ignition for this sample of approximately 0.15 percent. The only losses that exceeded this value were ignitions in 5 and 10% oxygen. The loss at 1050 °C in 10% oxygen with normal cooling was 0.166 to 0.172 percent. The loss at 1000 °C in 5% oxygen with normal cooling was 0.175 to 0.187 percent and with slow cooling was 0.141 to 0.154 percent. An easily reproducible ignition procedure to give a stoichiometric U_3O_8 or a procedure to give a reproducible oxide without using a controlled atmosphere could not be discovered, so; the procedure previously developed to give a reproducible oxide will continue to be used. This procedure is given below.

23

Table 6. Ignition loss of SRM 950a, Uranium Oxide (U_3O_8), with varying cooling rates.

Temperature C	Slow cooling % loss	Normal cooling % loss	Fast cooling % loss
850		0.076	
900	0.083	0.088	0.096
950	0.086	0.102	
1000	0.090	0.114	0.120
1050	0.094	0.126	

Samples of uranium oxide were placed in platinum boats formed from 0.002 inch platinum foil. The sample boats were placed in a quartz tube, the furnace moved over the sample area and the sample ignited overnight at 1050 °C in a dry, carbon dioxide free atmosphere of air. After cooling the furnace to 850 °C the samples were ignited in a pure oxygen atmosphere for 1 hour. The samples were cooled (normal cooling) and transferred to small glass desiccators for weighing. All weighings were done on a microbalance.

Although the procedure does not give stoichiometric U_3O_8, it does give a reproducible oxide [ref. 5, p. 68] which can be used for isotope dilution analyses.

C.   Plutonium Isotopic Standards

1.   Modification of Plutonium Analytical Procedure

The procedure for plutonium analysis [3] is closely patterned after the uranium procedure. Two major changes were made and the new technique has been labelled "provisional" until extensive testing is completed. The changes are a larger drying current during sample mounting and elimination of degassing.

Instead of an upper limit of 2 A for drying, the filaments were adjusted to 2.3-2.4 A for 1 minute to convert the sample to plutonium oxide. Heating the filament to a dull-red glow (∿2.5 A) was avoided. Several seconds of dull-red heat pro-

24

duced no apparent change in Pu^+ signal response, although there were some indications of reduced signal intensity.

During the degassing of a large number of plutonium samples it was observed that a significant Pu^+ signal (10^{-12} A) was not detected until the filament currents were between 1.7-2.0 A. After the sample was allowed to cool for 1/2 hour and was reheated to start the analysis, plutonium ion current intensity was usually more than 5×10^{-11} A at sample filament currents less than 1.5 A. Careful stepwise increases in the sample filament currents would burn-off the low temperature signal and eventually a growing and stable signal was obtained.

A limited number of analyses were made without degassing and it was observed that sample filament currents of approximately 2 A produced plutonium signals of $1-2\times10^{-11}$ A. The signal intensity increased slowly and the ion current emission was exceptionally stable. It appeared that the growth phase could be maintained for most of the time span necessary to measure the plutonium isotopic ratios. It is believed that with some additional development, analysis of plutonium samples without degassing will be a superior method to the present procedure patterned strictly after uranium analysis.

2. Half-life of ^{241}Pu

The evaluation of the half-life of ^{241}Pu was continued on both SRM 948, Plutonium Isotopic Standard, and a United Kingdom sample (UK-131) using the anion-exchange separation of americium from plutonium [ref. 6, p. 64]. The americium separation must be as nearly complete as possible to allow the ^{241}Pu content to be determined by mass spectrometry without interference by the ^{241}Am produced by the β decay of ^{241}Pu. The ^{241}Am content has been growing since it is produced from ^{241}Pu with a half-life less than 15 years and itself decays with a half-life of more than 400 years. The Radiochemical Analysis Section (310.01) used a counting technique to determine the ^{241}Am content on an aliquot of both SRM 948 and UK-131 samples that were also measured by mass spectrometry. Results

of the ^{241}Am gamma-ray measurements indicate no more than 0.002 ppm ^{241}Am in the two samples immediately after the ion-exchange separation. This means the ion-exchange separation is essentially complete and ^{241}Am did not affect the ^{241}Pu measurements by mass spectrometry.

The half life of ^{241}Pu calculated from the annual determination of the isotopic composition of SRM 948 and UK-131 was not significantly different from the value of 14.6±0.4 years given in the last annual report [4]. However, the variation of the value from year to year is greater than can be accounted for by either a background contribution from ^{241}Am remaining in the sample or by imprecision in the ratio measurements. The probable cause of this abnormal fluctuation has not been determined.

D. Assay of SRM 727, Rubidium Chloride

Standard Reference Material 727, Rubidium Chloride, is issued by the Office of Standard Reference Materials (OSRM) as an intermediate purity standard which has been assayed by silver coulometry for chloride and corrected for impurities. Since the material is intended primarily as a rubidium standard OSRM requested that this material be assayed for rubidium content.

During the course of the development of a chemical procedure for the recent redetermination of the atomic weight of rubidium [7], it was shown that rubidium perchlorate was an excellent weighing form for rubidium. The compound is stoichiometric and non-hydroscopic up to 90% relative humidity. When precipitated from solution, the only elements that accompany it are cesium and potassium. Also, during the analysis of the TEGs (see section 3-B) it was shown that small amounts of rubidium could be determined with adequate accuracy by isotope dilution mass spectrometry. Therefore, it was proposed to assay this material by a combination of gravimetry to determine most (99+%) of the rubidium as rubidium perchlorate

26

and isotope dilution mass spectrometry to determine the soluble rubidium in the filtrate from the precipitation.

Two bottles of SRM 727, Rubidium Chloride, marked Btl. I and Btl. II were received from OSRM for analysis. The material was dried in a desiccator over freshly exposed magnesium perchlorate for twenty-four hours. Four samples of about 2 grams each were taken from each bottle and weighed on a micro-balance.

Each sample was then assayed for rubidium by the following procedure. The sample was dissolved in about 70 cm^3 of water in a 100 cm^3 teflon beaker. About 2-5 cm^3 of "ultra-pure" perchloric acid was added and the solution was heated until all of the rubidium perchlorate dissolved. The solution was slowly evaporated to fumes of perchloric acid and then at higher heat to dryness. After cooling, the rubidium perchlorate was dissolved in about 50 cm^3 of water by heating the solution. This solution was slowly evaporated to about 10 cm^3 to crystallize most of the rubidium as rubidium perchlorate. After cooling the solution, 0.5 cm^3 of perchloric acid was added and the beaker and contents were cooled to about 5 °C to reduce the solubility of rubidium perchlorate. The crystallized rubidium perchlorate was caught in a medium porosity, 15 cm^3 glass filtering crucible, washed with 95% ethanol and the filtrate was reserved for the determination of soluble rubidium. The crucible and contents were dried at 100 °C for four hours, covered with a platinum cover and further dried by slowly increasing the temperature to 300 °C to remove occluded mother liquor. The crucible and contents were kept at this temperature for 16 hours, then cooled and weighed on a micro-balance. The heating at 300 °C, cooling and weighing were repeated until a constant weight was reached, that is until the weighings agree to within 20 µg. The air weight of rubidium perchlorate was converted to vacuum weight.

The weighed rubidium perchlorate was corrected for potassium and cesium perchlorates in the following manner. The

27

potassium in the rubidium perchlorate was determined by isotope dilution mass spectrometry after thermally converting the rubidium perchlorate to rubidium chloride in a covered quartz crucible at 600 °C. This material was dissolved in water and transferred to a tared 100 cm³ polyethylene bottle and diluted to 100 cm³. The solution was mixed and the bottle and contents were weighed to ±0.1 mg. A weighed aliquot of about 10 g of this solution was spiked with [41]K to produce an altered [39]K/[41]K ratio of about 1, based on prior analysis of potassium in the original rubidium chloride. This solution was diluted so that 1 cm³ of solution contained 1 mg natural rubidium (0.5 µg spiked potassium) and the [39]K/[41]K ratio was determined. The mass spectrometric procedure described (see section 3B) for potassium was followed with a downward adjustment in total potassium signal intensity in proportion to the smaller sized sample (of potassium) being loaded. The large excess of rubidium present generated a significant amount of scattered background at the potassium mass positions. This background varied with mass and grew in proportion to the signal growth. All the potassium determinations were made on signals which grew slowly and linearly. Background corrections were made to the peak heights and amounted to only 1 to 2 percent of the total. The amount of potassium in the aliquot was then calculated and from this, the weight of potassium perchlorate in the rubidium perchlorate was calculated. The amount of cesium in the original rubidium chloride was only 24 ppm and almost all of this would precipitate with the rubidium perchlorate so a correction for cesium was calculated from this value.

The solubile rubidium in the filtrate from the rubidium perchlorate filtration was determined by isotope dilution mass spectrometry. The filtrate was evaporated to fumes of perchloric acid, taken up with about 50 cm³ of water, transferred to a tared 100 cm³ polyethylene bottle and diluted to 100 cm³ after the addition of 2 cm³ of hydrochloric acid. A weighed portion of about 5 g was spiked with a weighed amount of [87]Rb

solution to produce an altered $^{85}Rb/^{87}Rb$ ratio of about 0.3.
The solution was evaporated to dryness and taken up with (1+49)
hydrochloric acid so that 1 cm^3 contained about 10 µg rubidium.
The $^{85}Rb/^{87}Rb$ ratio was then determined. The mass spectro-
metric procedure used was identical to the method previously
developed for rubidium chloride [ref. 4, p. 32]. The tempera-
ture used in drying the samples on the sample filaments is high
enough to convert rubidium perchlorate to rubidium chloride.
Test samples using natural rubidium perchlorate responded the
same as the chloride and gave the same isotopic ratios. The
amount of rubidium in the portion was calculated and, from
this value, the total rubidium in filtrate was determined.

Because of the small amount of rubidium in the filtrate
and also the low level of potassium coprecipitated with the
rubidium, the total assay of the rubidium is relatively insen-
sitive to errors in both determinations. An error of 1 percent
in the determination of rubidium in the filtrate or of 10
percent in the coprecipitated potassium will cause less than
1 part in 15,000 error in the total assay.

The total rubidium in the sample was determined from the
sum of the corrected rubidium from the gravimetric determina-
tion of rubidium perchlorate and the rubidium found in the
filtrate by isotope dilution analysis.

The results of the assay of four samples from each of
the two bottles are shown in Table 7. The material assayed
99.896±0.019 percent rubidium chloride.

This procedure was first applied to a high-purity sample
of rubidium chloride in which the only detected impurities
were 24 ppm potassium, 5 ppm magnesium, and <10 ppm cesium.
Ten fused samples of 1.7 to 2.2 g of this rubidium chloride
were assayed as described. This material assayed 99.979±0.012
percent. The results are reported in Table 8.

Table 7. Assay of SRM 727, Rubidium Chloride.

Sample no.	Wt RbClO$_4$ found g	KClO$_4$ corr mg	CsClO$_4$ corr mg	Corrected wt RbClO$_4$ g	Rb from RbClO$_4$ g	Rb from filtrate mg	Total Rb found g g	Wt RbCl taken g	Rb calc from RbCl g	Assay %
Btl I										
1	2.854386	2.225	0.078	2.852083	1.318287	4.196	1.322483	1.872936	1.323808	99.900
2	2.705699	2.020	0.074	2.703605	1.249658	3.168	1.252826	1.774243	1.254051	99.902
3	2.858400	2.314	0.079	2.856007	1.320101	3.757	1.323858	1.875078	1.325322	99.889
4	2.699425	2.023	0.074	2.697328	1.246756	2.821	1.249577	1.769482	1.250686	99.911
Btl II										
5	2.913445	2.528	0.080	2.910837	1.345444	2.910	1.348354	1.909768	1.349841	99.890
6	3.055682	2.482	0.084	3.053116	1.411208	2.336	1.413544	2.001986	1.415022	99.896
7	3.003090	2.258	0.083	3.000749	1.387003	6.660	1.393663	1.973820	1.395114	99.896
8	2.946327	2.498	0.081	2.943748	1.360656	3.734	1.364390	1.923638	1.366006	99.882

Average 99.896

s.d. $\pm$ 0.008

95% C.L. $\pm$ 0.019

Table 8. Assay of high–purity rubidium chloride.

Sample no.	Wt RbClO$_4$ found g	KClO$_4$ corr mg	Corrected wt RbClO$_4$ g	Rb from RbClO$_4$ g	Rb from filtrate mg	Total Rb found g	Wt RbCl taken g	Rb calc from RbCl g	Assay %
1	2.636810	0.178	2.636632	1.218701	21.582	1.240283	1.755332	1.240684	99.968
2	2.934184	0.198	2.933986	1.356144	47.797	1.403941	1.986803	1.404290	99.975
3	2.951246	0.199	2.951047	1.364030	11.504	1.375534	1.946564	1.375849	99.977
4	2.922692	0.197	2.922495	1.350833	5.396	1.356229	1.919250	1.356543	99.977
5	2.716100	0.183	2.715917	1.255348	1.381	1.256729	1.778316	1.256962	99.981
6	2.724162	0.184	2.723978	1.259074	7.200	1.266274	1.791803	1.266462	99.985
7	3.341109	0.226	3.340883	1.544220	3.584	1.547804	2.190426	1.548213	99.974
8	3.091761	0.209	3.091582	1.428988	9.332	1.438320	2.035625	1.438772	99.969
9	3.020074	0.204	3.019870	1.395841	4.632	1.400473	1.981903	1.400827	99.975
10	2.729990	0.184	2.729806	1.261768	4.961	1.266729	1.792561	1.266998	99.979
								Average	99.979
								s.d.	± 0.005
								95% C.L.	± 0.012

31

SRM 727, Rubidium Chloride was originally issued as an intermediate purity chemical. After the completion of this work on the assay of rubidium the material was redesignated as SRM 984, Rubidium Chloride, and is certified for assay and absolute isotopic composition.

A copy of the certificate for SRM 984 is included as Appendix I.

E.   Assay of Potassium Chloride

The Office of Standard Reference Materials plans to issue a high-purity potassium chloride as a standard for both potassium and chloride. They have requested that a assay procedure for potassium in this material be developed.

A preliminary investigation has shown that a procedure based on the precipitation of potassium perchlorate followed by isotope dilution determination of soluble potassium can be used for the high accuracy assay of this material.

32

3. TRACE CHARACTERIZATION BY ISOTOPE DILUTION ANALYSIS

A. Methodology

1. Introduction

Mass spectrometric isotope dilution analysis is a powerful tool for the determination of trace level constituents in materials. The method consists essentially of the following steps:

a) The addition of a weighed portion of a separated isotope solution of known concentration to a known weight of sample;

b) Dissolution of the sample by appropriate means and thorough mixing of the resulting solution to ensure equilibrium of the separated isotope with the impurity element;

c) Chemical extraction of the isotopically altered impurity element;

d) Mass spectrometric measurement of the altered isotopic ratio; and,

e) Calculation of the amount of impurity element present in the sample.

The major advantages of the technique are the high accuracy attainable (better than 1 percent for most elements with some elements at the 0.1 percent level) and the fact that chemical separation and recoveries need not be quantitative.

The major disadvantages of the method is the problem of facility and reagent contamination or blank. This difficulty is common to all trace methods with the exception of activation analysis. Since the amount of the blank limits the lower range of trace element determination, considerable effort was focused on this problem. The facilities blank for such elements as lead and potassium has been lowered by carrying out chemical operations such as dissolution and evaporations in a Class 100 clean air hood. The reagent blank has been lowered by selection of high-purity reagents for the lowest contamination of the elements to be determined or by in-house

33

purification by isothermal distillation. Lead blanks for the
analysis of lead in glass standards were in the range 1 to
2 µg when the analyses were carried out in the normal air of
the laboratory. This lead blank has been reduced to 0.02 µg
by carrying out the chemical operations in a Class 100 clean
air hood. Potassium blanks that were as high as 7 µg for the
analysis of potassium in the glass when carried out in normal
laboratory air have been reduced to 0.4 µg.

    2.   <u>Storage of Separated Isotope Solutions and Method of</u>
         <u>"Spiking"</u>

Solutions of separated isotopes are stored either in
boro-silicate glass flasks or in teflon bottles. The glass
flasks are constructed from 200 cm³ volumetric flasks by
cutting the neck of each flask about 1 cm from the body and
tooling the neck for a serum stopper closure. These flasks
are stoppered with rubber serum septa and sealed with crimped
aluminum caps and are stored in desiccators containing a little
water to maintain 100% relative humidity on the outside of the
flasks. Solutions stored in this manner have shown virtually
no change in weight over a 1 year period.

Solutions of separated isotopes which could be contamina-
ted by boro-silicate glass are stored in 200 cm³ teflon
bottles. While storage in teflon has not been as satisfactory
as in glass, in no case was the weight loss of a solution
greater than 0.1 percent for a three month period.

The "spiking" for isotope dilution analysis is done by
weight. A 4-inch platinum or stainless steel needle with a
Kel-F hub is inserted thru the septum closure into the solution.
A second needle which just punctures the septum serves as a
vent. A polyethylene hypodermic syringe of appropriate size
is attached to the hub of the needle. (The rubber plunger of
the syringe is covered with teflon by streching a small piece
of 7.5 mil thick teflon over it.) The desired amount of
solution is drawn into the syringe, the syringe is disconnected

from the needle hub, and the tip is capped with a Kel-F cap. Any static charge that might be present is dissipated by wiping the syringe with a damp paper towel. The syringe and contents are then weighed on a semi-micro balance to ±0.02 mg. The spike solution is delivered from the syringe to a beaker containing the material to be analyzed and the syringe is again capped, wiped, and weighed. The weight of the spike solution is determined from the weight of the syringe before and after delivery of the solution. This method of separated isotope spiking permits the delivery of 1 g (1 cm^3) of spike with less than 0.01 percent uncertainty.

3. Spike Calibrations

The concentration of a separated isotope solution is determined by the addition of a known amount of the natural element (preferably a SRM of known assay) to a weighed portion of the spike solution. The isotopic abundance ratio of the element is then measured by mass spectrometry and the concentration of the separated isotope solution is calculated.

This is a necessary procedure since separated isotopes are normally furnished as compounds which are of unknown total purity.

B. Trace Elements in Glass SRMs

The Office of Standard Reference Materials has prepared four glass SRMs in the form of wafers cut from glass canes which have been doped with 61 elements at the 500 ppm, 50 ppm, 1 ppm and 0.02 ppm levels, respectively. Lead, silver, copper, thallium, potassium, rubidium and uranium were determined by isotope dilution mass spectrometry in the 500 ppm and 50 ppm standards and, with the exceptions of copper and silver, the same elements were determined in the 1 ppm and the 0.02 ppm standards. Wafers about 1 mm thick and weighing about 0.3 g were used for the analysis of the 500 ppm standard and wafers about 3 mm thick and weighing about 1 g were used for the analysis of the other standards. Uranium was determined in

separate samples while the other elements were determined by multiple spiking of the same sample.

   1.   Multiple Spiking Procedure and Determination of
        Silver, Copper, Potassium, Lead, Rubidium and Thallium

        a.   Sample preparation, spiking and dissolution -
Each wafer was cleaned by wiping with a paper towel saturated with ethanol and by immersion in (1+9) nitric acid for 5 minutes to remove surface contamination. The wafers were then washed with distilled water, air dried, and weighed.

   Each weighed wafer was transferred to a 30 cm³ teflon beaker and a appropriate amount of ^{65}Cu, ^{206}Pb, ^{41}K, ^{87}Rb, ^{109}Ag, and ^{203}Tl spike solutions were added to each sample, except that ^{65}Cu and ^{109}Ag were not added to the 1 ppm and the 0.02 ppm standards. These separated isotope solutions were calibrated by using SRM 976, Copper Isotopic Standard, for the spike calibration of the ^{65}Cu solution; SRM 981, Natural Lead Isotopic Standard, for the spike calibration of the ^{206}Pb solution; high purity (99.99+%) natural potassium chloride for the spike calibration of the ^{41}K solution; SRM 984, Rubidium Isotopic Standard, for the spike calibration of the ^{87}Rb solution; high purity natural silver (99.99%) for the spike calibration of the ^{109}Ag solution; and high purity natural thallium for the spike calibration of the ^{203}Tl solution.

   Three blanks were prepared by adding the same spike solution to beakers without samples. Throughout this procedure these blanks were treated exactly as the sample solutions. The glass wafers were dissolved by treating each sample with 10 cm³ of (1+1) hydrofluoric acid and 5 cm³ (2 cm³ for the 1 ppm and 0.02 ppm standards) of perchloric acid. The beakers were covered with teflon covers and placed on a hot plate at low temperature for about 16 hours. The skeletons remaining from the dissolution were crushed with teflon rods and the wafers were allowed to react further if not completely dissolved. (A considerable quantity of insoluble CaF_2 was produced during the dissolutions, but this material had a different

36

appearance from the wafer.) The solutions were then slowly evaporated to fumes of perchloric acid to volatilize SiF_4 and to convert insoluble CaF_2 to soluble $Ca_3(ClO_4)_2$. The sides of each beaker were washed with water, 1 cm^3 of hydrofluoric acid was added, and the evaporation repeated to strong fumes of perchloric acid.

   b.   Separation of lead and thallium - Lead and thallium were separated from the sample solutions by electro-deposition. Two different electrodeposition procedures were used depending on the amount of lead present. The method used for the 500 and 50 ppm standards (high acid) gave unsat-isfactory recoveries of lead when less than 10 μg of lead was present. The electrochemical method described for the 1 and 0.02 ppm standards (low acid) is based on the work of H. Müller [8] and was found to give satisfactory recoveries (>70%) with as little as 1 μg of lead. This method is the method of preference and would be used if the analysis of the 500 and 50 ppm standards were repeated.

   Each solution from the dissolution of the 500 ppm and the 50 ppm samples were treated as follows: The solution was diluted to about 25 cm^3 and 1 cm^3 of nitric acid was added. The solution was then electrolyzed at 0.02 A (about 2 volts) using 50 mil platinum wires for both anode and cathode. The solution was stirred magnetically during the electrolysis which was continued for at least six hours. Lead and thallium were deposited on the anode as PbO_2 and Tl_2O_3. Copper and silver were deposited on the cathode as copper and silver metal. The sample solutions were reserved for the determina-tions of potassium and rubidium.

   The platinum anode containing the electrodeposited PbO_2 and Tl_2O_3 was weighed on a micro-balance and the deposit was stripped from the electrode with a few cm^3 of a dilute nitric acid-hydrogen peroxide mixture. The resulting solution was evaporated to dryness and taken up with sufficient (2+98) nitric acid so that the solution contained about 200 μg lead

37

and 200 µg thallium per cm^3 and reserved for mass spectro-
graphic analysis.

Each solution from the dissolution of the 1 and 0.02 ppm
standards was treated as follows: The solution was evaporated
to dryness, taken up in a few cm^3 of water, and again evapo-
rated to dryness. The residue was then taken up with 10 cm^3
of water and 1 cm^3 of a 0.5N nitric acid solution to which
1 mg of copper had been added. The solution was then electro-
lyzed at 0.02 A (about 2 volts) using 50 mil platinum wires
for both anode and cathode. (The copper is added to convert
the platinum cathode to a copper cathode which prevents the
formation of nitrous acid.) The solution was stirred magneti-
cally during the electrolysis which was continued for at least
six hours. The cathode was then washed with water and the
PbO$_2$ and Tl$_2$O$_3$ was stripped from the electrode with a dilute
nitric acid-hydrogen peroxide mixture. After evaporation,
the residue was taken up with one drop of (2+98) nitric acid
and reserved for mass spectrometric analysis.

c. <u>Determination of lead and thallium</u> - The mass
spectrometric procedure used for the lead analyses was the
silica gel technique which is described in a later section
(section 4, below).

The results of these determinations are shown in Table 9.

As with all analyses of very small lead samples, constant
vigilance is required to prevent abnormally large blanks. In
this series the original laboratory blanks were of the order
of 2 µg. With the use however of "ultra pure" reagents and
of small Class 100 laminar flow "clean hoods" for all dissolu-
tion and filament mounting steps the laboratory blank was
reduced to ~0.02 µg.

If thallium was to be determined on the same filament
loading a short addition to the lead procedure was used. The
filament current was increased slowly until a thallium grid
signal of 3×10^{-10} A was obtained. After 1 minute the current

38

Table 9. Determination of lead in TEG standards.

500 ppm TEG

Position	ppm Pb
2	426.48
13	426.17
18	425.56
48	426.09
56	426.86
66	426.00
78	426.21
106	426.68

Average 426.13

s.d. ± 0.42

95% C.L. ± 1.02

Ave. blank correction ~ 0.8 ppm

50 ppm TEG

Position	ppm Pb
2	38.57
37	38.68
44	38.64
68	38.51
75	38.41
114	38.62

Average 38.57

s.d. ± 0.09

95% C.L. ± 0.23

Ave. blank correction ~ 0.3 ppm

1 ppm TEG

Position	ppm Pb
2	2.35
36	2.41
40	2.35
69	2.37
76	2.38
114	2.33

Average 2.36

s.d. ± 0.03

95% C.L. ± 0.07

Ave. blank correction ~ 0.02 ppm

0.02 ppm TEG

Position	ppm Pb
2	1.87
33	1.89
43	1.90
51	1.86
61	1.88
76	1.88
130	1.89

Average 1.88

s.d. ± 0.02

95% C.L. ± 0.04

Ave. blank correction ~ 0.02 ppm

was reduced to give a grid signal of 5×10^{-11} A. The signal was allowed to stabilize for 5 minutes after which ten ratios were measured.

The results of the thallium determinations are given in Table 10.

Table 10. Determination of thallium in TEG standards.

500 ppm TEG

Position	ppm Tl
2	63.58
13	60.17
18	61.47
48	61.19
56	62.27
66	61.40
78	62.26
106	61.95

Average 61.79

s.d. $\pm$ 1.00

95% C.L. $\pm$ 2.37

50 ppm TEG

Position	ppm Tl
2	15.66
37	15.81
44	15.75
68	15.59
75	15.54
114	15.73

Average 15.68

s.d. $\pm$ 0.09

99 95% C.L. $\pm$ 0.23

1 ppm TEG

Position	ppm Tl
40	0.270
76	0.269
114	0.268

Average 0.269

s.d. $\pm$ 0.001

95% C.L. $\pm$ 0.005

0.02 ppm TEG

Position	ppm Tl
33	0.00834
43	0.00809
76	0.00818

Average 0.00820

s.d. $\pm$ 0.00013

95% C.L. $\pm$ 0.0005

d. Separation of copper and silver – The isotopi-
cally altered copper and silver were separated from the sample
solution of the 500 and 50 ppm standards by electrodeposition
as described under the separation of lead and thallium. The
silver and copper were then separated from each other as
follows: The platinum cathode containing the silver and
copper was treated with 5 cm³ (1+9) nitric acid to strip the
silver and copper from the electrode. The resulting solution
was diluted to 25 cm³ and silver was electrodeposited onto a
50 mil platinum cathode at a cathodic potential of 0.242
(0.0V vs S.C.E.). The solution was stirred magnetically and
the electrolysis was continued for at least 6 hours. The

cathode was then washed with water followed by ethanol, dried
and weighed. The silver was then stripped from the electrode
with (2+98) nitric acid and the resulting solution was evapo-
rated to dryness. The residue was taken up with (2+98) nitric
acid so that the solution contained 500 µg Ag/cm^3 and this
solution was reserved for the mass spectrometric measurement
of the altered $^{107}Ag/^{109}Ag$ ratio.

Copper was electrodeposited onto a 50 mil platinum wire
cathode from the solution remaining from the silver separation
at -0.4V cathode potential (vs S.C.E.) The solution was
stirred in the same manner and the electrolysis was continued
for at least 6 hours. The cathode was washed with water
followed by ethanol, dried, and weighed. The copper was then
stripped from the electrode with (2+98) nitric acid and the
resulting solution was evaporated to dryness. The residue was
taken up with sufficient (2+98) nitric acid so that the solu-
tion contained 500 µg Cu/cm^3 and this solution was reserved
for the mass spectrometric measurement of the altered
$^{63}Cu/^{65}Cu$ ratio.

    e. Determination of copper - The analytical pro-
cedure presently used for all copper isotope dilution analyses
is basically the same technique described for small amounts of
copper (∿20 µg) in a previous report [4]. The source material
from which copper is extracted is relatively unimportant but
the total amount of copper provided for analysis and the purity
of the solution is critical. The chromium, potassium and
sodium from the sample and filament material must be maintained
at levels so that they will decay below critical limits within
the first 25 minutes of filament heating. Large chromium ion
currents will produce significant baseline interference near
or at the ^{63}Cu mass position. Once the solution requirements
are satisfied the key to precise analysis is filament tempera-
ture control and adherance to a strict time schedule.

    Periodic use during the past year has indicated that for
most analyses the internal change in the $^{63}Cu/^{65}Cu$ ratio can

be held to approximately 0.5 percent. There is a loss in
analytical precision when the copper ion current ratio of
altered samples is greater than 5:1. Similarly, there is
increased difficulty in measuring the large ion current ratios
of separated isotope solutions and blank samples of the
smaller sample size.

The Cu^+ ion currents were measured on a single stage solid
sample mass spectrometer with a 6-inch radius of curvature-60°
analyzer tube and a "Z" lens ion source. A triple filament
rhenium ribbon source was used and the ion accelerating
voltage was 7.5 KV.

One drop of copper nitrate solution (0.5 mg Cu/cm^3) was
placed on each sample filament. The copper was electroplated
onto the filaments at a potential difference between the
platinum wire and the filament of 3.5 volts. The current was
approximately 1 mA and was maintained for 10 minutes. At the
conclusion of the plating cycle and with the current ON, the
remaining solution was flushed from the filaments with a
stream of alcohol. This step was taken to prevent redissolving
of plated copper by the nitric acid solution on the filament.
The estimated sample size was 10 μg. The filaments were
mounted in the filament block with the sample filaments
positioned away (∿0.025 inch) from the edges of the ionizing
filament. The open spacing technique was used to inhibit
sample evaporation by radiant heat from the ionizing filament.

An optical pyrometer was used to measure filament tempera-
tures. During the first minute of heating the ionizing filament
temperature was adjusted to 2120 °C (5.5-6.0 A) and the sample
filament currents were set at 0.5 A. After 5 minutes of heat-
ing the sample filaments were increased until the total copper
ion current was 4×10^{-14} A. The ionizing filament temperature
normally decreased significantly during the first 10 minutes
of heating but began to stabilize at approximately 2100 °C.

After 15 minutes of heating the signal will have normally
increased to approximately 1×10^{-13} A. The temperature of the

42

ionizing filament was checked and, if necessary, was adjusted to 2100 °C. The sample filament currents were increased to yield a total signal intensity of $2.7-3.0\times10^{-13}$ A. During the next 10 minutes it was necessary to focus the signal for maximum intensity and mass scan to determine baselines of ^{63}Cu and ^{65}Cu. The ion current was expected to be $4-5\times10^{-13}$ A and growing.

Twelve peak sets of data were taken between 25 and 38 minutes after the start of heating. Each peak top was monitored for 30 seconds and the magnet current changes were made in discrete steps. The analysis was concluded with another mass scan to determine baselines of $^{63}Cu/^{65}Cu$. Each analysis consisted of two sets of six ratios each. The average of the first six ratios were used as data and the average of the second set of six ratios was compared with the first to determine the point on the fractionation curve at which the data was taken.

The results of the determination of copper in the 500 ppm and the 50 ppm TEG standards are given in Table 11.

Table 11. Determination of copper in TEG standards.

500 ppm TEG		50 ppm TEG	
Position	ppm Cu	Position	ppm Cu
2	440.8[a]	2	37.32
13	443.8	37	37.74
18	443.2	44	37.59
48	444.6	68	38.05
56	445.4	75	37.67
66	442.5	114	37.93
78	444.6	Average	37.72
106	445.9	s.d. $\pm$ 0.36	
Average	443.9	95% C.L. $\pm$ 0.92	
s.d.	$\pm$ 1.7		
95% C.L.	$\pm$ 4.0		

[a] The precision of the method indicates some heterogeneity in this sample for this element.

Normally the signal intensity for most analyses can be expected to grow for at least 40 minutes. The magnitude of the filament bias correction was determined by monitoring the change in $^{63}Cu/^{65}Cu$ ratio between the first and second half of an analysis. Filament bias corrections were applied as follows: 1.1 percent when the ratio changed less than 0.3 percent; 0.9 percent when the ratio changed between 0.3 and 0.5 percent; 0.75 percent when the ratio changed 0.6 percent. Analysis in which the signal decayed before the end of the first set of 6 ratio measurements usually displayed gross fractionation (>1%) and all such analyses were terminated because of the difficulty in precisely determining the magnitude of the bias.

All filaments before use were degassed at 4 A for 1 hour in a vacuum and under a potential field. The trace copper background in the filament material decayed rapidly and was not detectable at a 10^{-15} A ion current sensitivity. There was a detectable chromium signal from degassed filamants but it was too small to produce significant baseline interference at the ^{63}Cu mass position.

Cross contamination between samples of different isotopic composition was not observed. The precaution of cleaning the source for blank determinations and analysis of separated isotopes of copper was always followed to further minimize possibility of memory effects.

f. Determination of silver - The basic analytical procedure for silver is described in a previous report [3]. Adaptations of the base procedure have been successfully used to analyze quantities of silver from 200 µg to 5 µg. The technique is essentially independent of the source material from which silver is extracted but it must be modified according to the total amount of sample available for analysis. As the sample size decreased the signal intensity must be acquired and measured over shorter time spans. A relatively high concentration of an impurity in solution with silver requires

44

higher sample filament temperatures to produce a standard signal intensity. The net effect of higher temperatures is an increased rate of fractionation which will produce apparent differences in the isotopic composition. Therefore, it is essential to provide silver nitrate solutions of high, uniform chemical purity.

The analytical procedure developed for isotope dilution analyses of the TEG samples would yield sufficient ion current intensity from a 20 µg sample to measure the abundance ratio of a natural sample with an analytical precision between 0.15 and 0.25 percent. Because the intensity during an analysis is small ($4-6\times10^{-13}$ A) and restricted to a narrow limit, there is a significant reduction in precision when comparing ion currents different from 2:1. For a 20 µg sample size the large ion current ratios of blank samples are measured at greatly reduced precision. If it is necessary to determine the isotopic composition of separated isotopes as part of the dilution work, the analysis should be made using larger sample sizes or with more sensitive detection.

The Ag^+ ions were measured on a single stage solid sample mass spectrometer with a 6 inch radius of curvature 60° analyzer tube and a "Z" lens ion source. A triple filament rhenium-ribbon source was used and the ion accelerating voltage was 7.5 KV. The source and collector slit widths were 0.010 and 0.040 inch, respectively.

One drop of silver nitrate solution, 1 mg Ag/cm^3, was placed on each sample filament and dried for 5 minutes with a heat lamp and a 1 A current in an atmosphere of air. The filaments were placed in a hydrogen atmosphere and the silver nitrate reduced to metallic silver by increasing the current to 2.5-3.0 A. Normally, there was no detectable redness in the filament. The sample size was estimated to be 10 µg per filament. The sample filaments were positioned away (∿0.025 inch) from the edges of the ionizing filament. The open

spacing was used to minimize sample evaporation and ionization by radiant heat from the ionizing filament.

Ionizing filament temperatures were measured with an optical pyrometer. During the first minute of heating the temperature was set to 2120 °C and the sample filament currents at 0.25 A. The silver ion current was usually less than 1×10^{-13} A. The ionizing filament temperature decayed during the early stages of heating and eventually stabilized at approximately 2100 °C. Between 5 and 6 minutes after the start of heating the sample filament currents were increased to yield a total intensity of 0.8×10^{-13} A. Exclusive of a brief period of decay after this adjustment, the signal was expected to grow for the remainder of the analysis.

After 11 minutes of heating three options were available. No adjustments were made if the total signal intensity was approximately 2×10^{-13} A. If the total intensity was less than 2×10^{-13} A, the sample filaments were adjusted to achieve this level. The final option was termination of the analysis if the signal intensity was approximately 4×10^{-13} A. Analyses in which the total ion current reached this level after only 10-11 minutes of heating were considered to be overheated because, in general, the ion currents would eventually decay before the end of the ratio measurement. Such analyses usually exhibited greater than normal internal changes in the $^{107}Ag/^{109}Ag$ ratio.

The mass scan to determine baselines was commenced after 15 minutes of heating. The ratio measurement was started promptly after 20 minutes of heating on a growing signal of $4-5 \times 10^{-13}$ A. Ten peak sets of data were taken between 20 and 31 minutes after the start of heating. Each peak was monitored for 30 seconds and magnet changes were made in discrete steps. The analysis was concluded with a mass scan to determine baselines of the silver peaks.

The results of the determination of silver in the 500 ppm and the 50 ppm TEG standards are given in Table 12.

46

Table 12. Determination of silver in TEG standards.

500 ppm TEG		50 ppm TEG	
Position	ppm Ag	Position	ppm Ag
2	254.5	2	22.72
13	252.8	37	22.10
18	254.1	44	22.09
48	253.3	68	21.84
56	254.8	75	22.09
66	251.9	114	22.02
78	261.6[a]	Average	22.14
106	252.3	s.d.	± 0.30
Average	253.4	95% C.L.	± 0.77
s.d.	± 1.1		
95% C.L.	± 2.7		

[a] Omitted from average.

Even at constant temperatures the ^{107}Ag/^{109}Ag ratio decreases with time during an analysis. The magnitude of this change is less than 0.25 percent for a 200 µg sample under controlled conditions over a 20 minute period but is more than 0.5 percent for a 20 µg sample over the same time span. Similarly, sample sizes of 200 µg will yield growing ion currents of 10^{-12} A for at least 1 hour but a 20 µg sample will not normally yield growing ion currents of 10^{-13} A for more than 40 minutes of heating.

SRM 978, Silver Isotopic Standard, was analyzed to obtain an estimate of the difference in the observed abundance ratio for operation at two slightly different filament temperatures with the 20 µg sample. All parameters were held constant except the slight differences in temperature. For the Group I analyses, a total signal intensity of 4×10^{-13} A was used as an upper limit and was simply changed to a lower limit for the Group II analyses. The uncorrected ^{107}Ag/^{109}Ag ratios are given below for comparison.

	Group I	Group II
	1.0830	1.0806
	1.0837	1.0813
	1.0833	1.0811
	1.0827	1.0798
	1.0832	1.0808

All filaments before use were degassed at 4 A for 1 hour
in a vacuum and under a potential field. Silver was not
detected in the filament material at a 10^{-15} A ion current
sensitivity. Significant amounts of zirconium from either
the sample or the filament material will contribute to a
zirconium oxide ($^{91}Zr^{16}O$) background at the 107 mass position.
Zirconium oxide peaks are also observed at the 106, 108, 110
and 111 mass positions. Degassing will reduce the zirconium
content of the filament below critical levels and solutions
of high chemical purity eliminated background contributions
from the sample.

        g.   <u>Separation of potassium and rubidium</u> - Potassium
and rubidium were separated from each sample solution as
follows: The sample solution which was reserved from the
first electrolytic separation, was evaporated to dryness on
a hot plate. The residue was taken up with 5 cm^3 of water
and a mixture containing 2 cm^3 of nitric acid and 1 cm^3 of
hydrochloric acid was added. (The nitric-hydrochloric mixture
was added to oxidize the ammonium ion formed during the
electrolysis.) The solution was again evaporated to dryness
and taken up with 5 cm^3 of water. The potassium and rubidium
in the solution were precipitated by adding 1 cm^3 of a solu-
tion containing 1 mg of NH$^+$ ion to act as a sweep and using
the free acid of tetraphenyl boron (TPB) as precipitant. The
acid form of TPB was generated by passing 5 cm^3 of a 1 percent
sodium tetraphenyl boron solution through a strongly acidic
cation exchange column (Dowex 50×8), followed by 5 cm^3 of
water and allowing the effluent containing the free TPB acid

to drip directly into the sample solution. (The column was constructed from the barrel of a 5 cm³ polyethylene hypodermic syringe and contained about 2 cm³ of resin.) The beaker and contents were cooled to about 5 °C and allowed to stand at this temperature for about 2 hours. The solution was then filtered thru acid washed filter paper of close porosity and the mixed potassium, rubidium and ammonium tetraphenyl borates were washed with cold water. The mixed tetraphenyl borates were then dissolved from the paper by washing with small amounts of acetone (about 10 cm³ total). This solution was diluted to about 20 cm³ with water and passed thru a small cation exchange column containing about 2 cm³ of a strongly acidic cation exchange column (Dowex 50×8) to remove the tetraphenyl boron ion which passed thru the column as the free acid. The column was washed with water until the effluent was neutral. The K^+, Rb^+ and NH_4^+ ions were removed from the column by elution with 30 cm³ of 4N hydrochloric acid. The resulting solution was evaporated almost to dryness and the ammonium ion present was oxidized to nitrogen by adding 0.5 cm³ of nitric acid and evaporating to dryness. To insure the removal of nitrate, the residue was twice taken up with 0.5 cm³ of (1+1) hydrochloric acid and evaporated to dryness. The final residue was taken up in 10 cm³ of (2+98) hydrochloric acid and this solution was reserved for the measurements of the altered $^{39}K/^{41}K$ and $^{85}Rb/^{87}Rb$ ratios.

h. Determination of potassium and rubidium - The 500, 50, 1 and 0.02 ppm TEG samples were analyzed for rubidium using the mass spectrometry procedure previously described [ref. 4, p. 32]. Since the chemical separation of rubidium also yielded potassium, and potassium may be run mass spectrometrically under the same operating conditions as rubidium, a procedure was developed for measuring both elements from the same sample loading. In the method adopted the rubidium was run first, following the previously developed procedure. Immediately after collecting the rubidium data the mass range

was adjusted to potassium and ten peak sets were taken over the next 10 1/2 minutes. No adjustments were made to the ionization or sample filaments between the rubidium and potassium portions of the run.

A sample containing natural rubidium and potassium, both at the 10 μg/cm^3 level, was used to test the method. The potassium was found to yield approximately the same signal level as rubidium and followed the same pattern of signal growth and decay as rubidium. The signals for both elements were stable with no detectable changes in the isotopic ratio over the 10.5 minute period of data taking. Precision of better than 0.1 percent for the isotopic ratios between samples was found for both elements in the test mixture.

Blanks for both the chemical and mass spectrometric portions of the analyses were determined for both rubidium and potassium. Neither source of blanks was significant for rubidium even for the 0.02 ppm TEG sample. Blanks for potassium, however, were significant and persistent for both the chemistry and mass spectrometry portions of the analyses for all the concentration levels of TEG samples. Improvements in blank levels for both areas were obtained as the analyses progressed from the 500 ppm TEG to the 0.02 ppm TEG samples. Mass spectrometric blank contributions were smaller than the chemical blank, partly because improved mass spectrometric procedures could be applied to previously run samples to obtain improved results.

Mass spectrometric blank levels for potassium were lowered thru work done with the separated ^{41}K isotope via the following steps:

a) The ionization and sample filaments, which are normally vacuum degassed at 4 A for 1 hour, were stored in a covered plastic box in a Class 100 clean hood at all times. Filaments were used within ∿2 days of degassing.

b) The samples were loaded, dried and mounted on the filament block in the Class 100 clean hood. Sample pipets

50

were also stored in the clean hood. In general the exposure
of the sample and filaments to room air was held to the
minimum possible time.

c) The ^{39}K signal was measured after the ionization
filament was adjusted to 1450 °C (before the sample filaments
were heated) to assure that an acceptably low level of potas-
sium background was present from this source. At the end of
the run the sample filaments were turned off and ^{39}K and ^{41}K
peaks were measured. Corrections for potassium from the
ionization filament (if necessary) were based on these ratios.

Evaluation of mass spectrometric blank levels using the
preceeding precautions was obtained by measuring the ^{39}K/^{41}K
ratio (reported to be ∿0.0084) of the separated ^{41}K isotope
used as a spike. Sample loading of 1/20 cm^3 at 10 µg K/cm^3
concentrations yielded ^{39}K/^{41}K ratios high by as much as 0.001
to 0.002. This corresponds to a total blank of 0.5 to 1 ng of
^{39}K on the two sample filaments. Considering the ubiquitous
nature of potassium in the air and dirt, increasing the size
of sample loading (when possible) is the most practical means
of further lowering the effective mass spectrometric blank.
At present 1 mg K/cm^3 concentration are being used to load
samples for potassium isotope dilution analysis. At this
level, <0.5 percent blank error would be found in the ^{39}K/^{41}K
ratio for the ^{41}K used as a spike. For the spiked sample the
mass spectrometric blanks would be undetectable with 1 mg K/cm^3
sample concentrations.

The results of the determination of potassium in the four
glass standards are shown in Table 13. These results show
that further work is needed on the method, especially with
blanks. Although blanks which were as high as 7 µg have been
reduced to less than 1 µg they are not consistant. For example,
the lowest blanks were for the 1 and 0.02 ppm standards, but
they ranged from 0.42 to 0.92 µg.

Table 13. Determination of potassium in TEG standards.

500 ppm TEG

Position	ppm K
2	457.6
13	461.3
18	461.0
48	460.5
56	466.8
66	461.9
78	463.2
106	458.1

Average 461.3

s.d. $\pm$ 2.9

95% C.L. $\pm$ 6.9

50 ppm TEG

Position	ppm K
2	68.14
37	61.48
44	64.22
68	61.85
75	59.81
114	64.90

Average 63.40

s.d. $\pm$ 2.98

95% C.L. $\pm$ 7.65

1 ppm TEG

Position	ppm K
2	29.1
36	29.2
40	32.6
69	30.4
76	28.3
114	28.9

Average 29.8

s.d. $\pm$ 1.5

95% C.L. $\pm$ 3.9

0.02 ppm TEG

Position	ppm K
2	29.3
33	27.1
43	34.0[a]
51	27.3
61	29.7
76	28.0
130	27.7

Average 28.2

s.d. $\pm$ 1.1

95% C.L. $\pm$ 2.8

_____

[a] Omitted from average.

The results for the determination of rubidium in the four glass standards are shown in Table 14. Since rubidium is not a common element either in reagents or the atmosphere, the blanks were consistantly low (about 1 ng) and were not a limiting factor.

Table 14. Determination of rubidium in TEG standards.

500 ppm TEG

Position	ppm Rb
2	425.27
13	425.56
18	425.55
48	425.46
56	425.71
66	425.06
78	426.12
106	425.92

Average 425.71

s.d. ± 0.30

95% C.L. ± 0.69

50 ppm TEG

Position	ppm Rb
2	31.58
37	31.24
44	31.37
68	31.50
75	31.44
114	31.50

Average 31.44

s.d. ± 0.14

95% C.L. ± 0.37

1 ppm TEG

Position	ppm Rb
2	0.853
36	0.854
40	0.854
69	0.858
76	0.853
114	0.856

Average 0.855

s.d. ± 0.002

95% C.L. ± 0.005

0.02 ppm TEG

Position	ppm Rb
2	0.102
33	0.100
43	0.107
51	0.100
61	0.103
76	0.102
130	0.100

Average 0.102

s.d. ± 0.003

95% C.L. ± 0.006

2. Determination of Uranium in TEG

a. Introduction - The uranium content has been determined in the 500 [ref. 4, p. 24], 50, 1 and 0.02 ppm glasses by isotope dilution mass spectrometry using a "U-235" separated isotope for the spike. On the first determinations it was decided to do boron and uranium on the same samples after fusion with sodium carbonate. The boron was extracted [ref. 4, p. 22] and the uranium separated by ion exchange.

53

The blanks for this set were much higher than expected
(∿400 ng). While this blank can be tolerated on the 500 ppm
glass, the other glass samples, particularly the 1 and 0.02
ppm, require a smaller blank. The boron extraction was omitted
from the second set and the blank was reduced to 25 ng. Two
dissolution procedures were used on the first set of 50 ppm
glass samples. One was the sodium carbonate fusion used on
the 500 ppm glass and the second was a hydrofluoric-perchloric
acid dissolution. The uranium was separated by the ion ex-
change technique used on the 500 ppm glass. The blanks were
2 ng on the fusion and 1 ng on the acid dissolution. The
uranium in the second set on the 50 ppm glass and the 1 and
0.02 ppm glasses were determined using the acid dissolution
and a modified ion-exchange separation. The blank using this
procedure was 0.5 ng. Both procedures are given below.

       b. <u>Carbonate fusion</u> - The glass samples were crushed
and 0.6 to 1.0 g was fused with sodium carbonate. After the
melt was broken up in water, weighed aliquots of "U-235"
separated isotope solution were added. Nitric and hydrofluoric
acids were added, the solution evaporated to near dryness, and
after diluting with water, the solution was filtered into a
beaker containing boric acid. The solution was passed through
an ion exchange column containing a strongly acidic cation
resin, 6 mm by 7 cm. After washing the column with nitric
acid (1+150), the uranium and other cations held by the resin
were eluted with nitric acid (1+3). The solution was evapo-
rated to dryness, taken up in nitric acid (1+1), and the
uranium separated by elution through a strongly basic anion
exchange column, 5 mm by 7 cm. The uranium was removed with
nitric acid (1+49), the solution was evaporated to dryness and
the elution through the strongly basic anion exchange column
was repeated. The sample was evaporated to dryness and after
dissolving in nitric acid (1+19) the isotopic ratios were
determined by mass spectrometry.

c. <u>Acid dissolution</u> - The glass samples were cleaned in alcohol and dilute nitric acid, weighed and transferred to teflon beakers. Ten cm^3 of hydrofluoric acid (1+1) were added. Weighed aliquots of "U-235" separated isotope solution, using a plastic syringe, were added to the beakers. After adding 7 g of perchloric acid and covering, the beakers were heated on low heat until the glass wafers were decomposed. The solution was evaporated to near dryness, the sides were rinsed down with nitric acid (1+1) and the evaporation was repeated. The salts were dissolved in about 1 cm^3 of nitric acid (1+1) and passed through a strongly basic anion exchange column 6 mm by 7 cm. The column was washed with a small volume of nitric acid (1+1) and then the uranium was eluted with nitric acid (1+49). The solution containing the uranium was evaporated to dryness, taken up in a few drops of nitric acid (1+1) and again eluted through the anion exchange column as above. The uranium eluate was collected in a teflon beaker, evaporated to dryness and after dissolving in nitric acid (1+19) the isotopic ratios were determined by mass spectrometry.

d. <u>Determination of uranium in 500, 50 and 1 ppm TEG</u> - The extensive background in uranium analysis acquired over the past decade paid significant dividends during the determination of uranium concentrations in the TEGs. No major or significant innovations in the existing analytical procedures were necessary to complete work on the 500, 50 or 1 ppm TEGs. Before analyzing a set of samples at a given level it was necessary to: (1) determine an optimum size (2) choose an optimum signal intensity for the ratio measurement and (3) select a calibration standard to evaluate the filament bias.

Once the sample size is fixed, the task of the analyst is to select a signal intensity that will yield maximum analytical precision for the ion currents to be measured and still avoid gross fractionation of the isotopes. From past experience it was known that total uranium sample sizes of 100, 20 and 4 micrograms per analysis will readily yield ion currents of

55

5×10^{-10} A, 1×10^{-10} A and 2×10^{-11} A, respectively. Although all of these ion current intensities could be maintained for a much greater time than was necessary to complete an analysis, none was used as an optimum for the TEG solutions. The factor that weighted heavily against them was a smaller rate of fractionation at lower filament temperatures, and consequently lower intensities, that would satisfy the precision require-ments of the peak height determination. The general rule is to select the smaller rate of fractionation once the precision requirement of expanded scale peak height determintion has been fullfilled. The other major factor that influenced the choice of optimum signal intensities was a vast amount of experience at the 10^{-11} A range. The final decision was to use optimum sample sizes of 40, 20 and 4 micrograms for the 500, 50 and 1 ppm TEGs with corresponding signal intensities of $5-6\times10^{-11}$ A, $1.5-2.0\times10^{-11}$ A and 1×10^{-11} A.

For each set of TEG samples one or more of the uranium SRMs was used as a calibration standard of known $^{235}U/^{238}U$ value to evaluate the filament bias. For maximum precision and accuracy the calibration standard was always analyzed at the same sample size and approximate ratio as the spiked samples.

The U^+ ion currents were measured on a single stage solid sample mass spectrometer with a 12-inch radius of curvature, $68°$ analyzer tube and a "Z" lens ion source. A triple fila-ment rhenium ribbon source was used and the ion accelerating voltage was 10 KV. The source and collector slit widths were 0.010 and 0.028 inches, respectively.

Uranium was supplied for analysis as uranyl nitrate, evaporated to dryness, in a small teflon beaker. Approximately 10 minutes prior to mounting uranium on the filament, a (1+19) nitric acid solution was added to the beaker. The volume was adjusted so that one drop of solution would contain 1/2 of the optimum sample size for the analysis. One drop of solution was placed on each sample filament and dried with a heat lamp and an electrical current. The current was adjusted as follows:

1 A for 5 minutes; 1.3 A for 3 minutes; slowly increased until
the yellow-orange oxide was formed. Color changes were dif-
ficult to detect for less than 20 µg of uranium per filament.
As the quantity of uranium per filament approched 1 µg a
drying current of 1.9-2.0 A was used as an upper limit in
lieu of a visual color change.

The standard procedure after introducing a sample into
the mass spectrometer was a 15 minute degassing followed by a
minimum time of 1/2 hour for cooling and source pumping. When
the source pressure was $2-4 \times 10^{-6}$ torr, liquid nitrogen was
added to the source coldfinger and degassing was begun after
cryogenic pumping reduced the pressure below 4×10^{-7} torr. The
degassing procedure is as follows: adjust the ion accelerating
voltage to 8 KV; adjust the ionizing filament temperature to
2160 °C and the sample filament current to 1.5 A; increase
the sample filament currents to 1.9 A; turn off all filaments
after 15 minutes of heating.

The heating pattern or method of adjusting the filaments
to obtain a standard ion current intensity is basically the
same for all uranium sample sizes above 1 µg. If the amount
of uranium is significantly less than 1 µg, then it may be
necessary to take data on a condensed time schedule as soon as
a measurable signal is obtained. Once the signal intensity
for a given sample size was established, the sample filament
currents were adjusted to yield some fraction of the total
intensity on a definite time schedule. Each sample filament
was always adjusted to yield 1/2 of the prescribed intensity.
The general procedure used for the TEG samples is as follows:
adjust the ionizing filament temperature to 2160 °C and the
sample filament currents to 1.5 A; after 6, 12 and 18 minutes
of heating adjust the sample filament currents to yield 1/3,
2/3 and then full intensity respectively; focus for maximum
signal intensity after approximately 7 and 19 minutes of heat-
ing. If necessary, after 24 minutes of heating reset the
sample filaments to yield full intensity. Data were taken

between 30 and 41 minutes after the start of heating on an ion current that was normally growing. A mass scan was made to determine baselines both before and after the ratio measurement. Each peak top was monitored for 30 seconds and scanning was accomplished by a step-wise change in magnet current to focus ion currents on the faraday cage.

        e. <u>Determination of uranium in 0.02 ppm TEG</u> - Determination of the uranium concentration in the 0.02 ppm TEG standard by isotope dilution required the measurement of a $^{235}U/^{238}U$ ratio of $\sim$160. To keep from exceeding the linear response region of the vibrating reed electrometer for measurement of the ^{238}U, the ^{235}U signal was limited to $<3\times10^{-13}$ A, which in turn limited the ultimate accuracy for this concentration series to 2 to 3 percent (Tσ). Also, the determination of the uranium composition of the base glass required a measurement of the $^{235}U/^{238}U$ ratio on $\sim$0.05 µg of uranium. The minimum acceptable sample size for the triple filament uranium technique is 1-2 µg.

For these reasons, the 0.02 series was run on a double stage mass spectrometer employing two 90 degree 12 inch radius magnetic sectors, with a pulse counting detection system. This instrument has been described in detail [1].

A filament loading technique was adopted from Dietz [9] and subsequently used for the 0.02 ppm samples. The dry samples were dissolved in several drops of nitric acid (1+19) and an estimated 0.1 µg deposited on a 50 mil rhenium V filament which had been previously degassed at $\sim$2000 °C. The sample was then dried under an infra-red heat lamp for 20 minutes.

An initial filament temperature of 1400 °C was used and was increased in 50° steps at 5 minute intervals to 1550 °C. At <1550 °C the uranium signal decayed regularly. Successive temperature increases of 25°/step usually produced a moderately growing ^{235}U signal of 50-60,000 counts per second. Around 1600 °C the signal intensity varied strongly with a small (25°) temperature change. For this reason, an optimum temperature

range of 1575-1625 °C was used with the several samples so that count rates of approximately 60,000 counts per second for each of the samples could be maintained.

To provide a fractionation correction factor for the 0.02 ppm series, SRM U-970 whose $^{235}U/^{238}U$ ratio approximated that of the samples was run. A correction factor of 0.9940 was applied to all experimental ratios.

The uranium oxide contribution to the ion beam normally decayed rapidly during the first few minutes of an analysis, to a final U^+/UO^+ ratio of >1000. Occasionally an incompletely degassed filament resulted in copious quantities of uranium oxide. These runs were discarded. Since the ionization efficiency and thus sensitivity appears to be considerably greater for the oxide, the oxide beam was temporarily considered for analysis. However, the signal intensity per quantum of sample was not reproducible.

The results on the four glasses are given in Table 15. The results indicate that the samples are homogeneous within experimental error except position 114 of the 50 ppm glass. The second set on the 50 ppm glass (Table 16) was run to verify the value found on position 114 and to determine the extent of the indicated inhomogeneity. The data show that the uranium content at position 114 is greater but, that the inhomogeneity does not extend into the region to be used for the SRM (positions 30 through 90).

Both procedures appear to give satisfactory results. The acid procedure requires somewhat less time and seems to give slightly lower blanks. The acid procedure also eliminates the possibility of contamination in the crushing of the sample.

Table 15. Determination of uranium in TEG standards.

500 ppm		50 ppm	
Position	ppm U	Position	ppm U
2	461.6	2	37.35
13	461.8	37	37.37
18	461.3	44	37.36
48	461.2	68	37.36
56	462.2	75	37.41
66	461.2	90	37.41
106	461.6	99	37.42
		114	37.66[a]
Average	461.6	Average	37.38
s.d.	± 0.4	s.d.	± 0.03
95% C.L.	± 0.9	95% C.L.	± 0.07

1 ppm TEG		0.02 ppm TEG	
Position	ppm U	Position	ppm U
2	0.8242	2	0.07149
36	0.8234	33	0.07077
40	0.8219	40	0.07155
69	0.8226	51	0.07225
114	0.8230	61	0.07208
		76	0.07163
		130	0.07208
Average	0.8230	Average	0.07169
s.d.	±0.0009	s.d.	±0.00050
95% C.L.	±0.0024	95% C.L.	±0.00123

_____

[a] Omitted from average.

60

Table 16. Determination of uranium in 50 ppm TEG standard.

Position	Method	Set 1 ppm U	Set 2 ppm U
2	Na_2CO_3	37.35	
37	Na_2CO_3	37.37	
44	Na_2CO_3	37.36	
68	Na_2CO_3	37.37	
68	$HF-HClO_4$	37.34	
75	Na_2CO_3	37.38	
75	$HF-HClO_4$	37.40	
75	$HF-HClO_4$		37.44
90	$HF-HClO_4$		37.41
99	$HF-HClO_4$		37.40
99	$HF-HClO_4$		37.43
114	Na_2CO_3	37.63[a]	
114.	$HF-HClO_4$		37.67[a]
114	$HF-HClO_4$		37.68[a]
	Average	37.37	37.42

[a] Omitted from average, the precision of method indicates sample heterogeneity at sample point 114.

C. <u>Iron and Steel Standard Reference Materials</u>

A number of iron and steel SRMs were analyzed for copper by isotope dilution mass spectrometry and a few were analyzed for nickel. These determinations were usually undertaken as a "referee" method to settle disputes between NBS and cooperating laboratories or between laboratories at NBS.

1. <u>Determination of Copper</u>

The procedure for the determination of copper in iron and steel SRMs is outlined in last years Summary of Activities [ref. 4, p. 26]. For material of high copper content (greater

than 0.5%), samples no smaller than 100 mg were taken, and the
solution resulting from the dissolution of the sample was
aliquoted by weight to obtain a homogeneous sample small
enough to "spike".

The results of these analysis are shown in Table 17.

Table 17. Determination of copper in various SRM steels.

SRM	Cu wt %	Average and estimate of 95% C.L.	SRM	Cu wt %	Average and estimate of 95% C.L.
125b	0.07112		1148	0.9891	
	0.07153			0.9885	
	0.07136			0.9896	
		0.07134 ± 0.00071			0.9891 ± 0.0099
1134	0.07100		1149	0.4880	
	0.07131			0.4865	
	0.07077			0.4902	
		0.07103 ± 0.00071			0.4882 ± 0.0049
1140	0.09550		361	0.04203	
	0.09586			0.04210	
	0.09641				
		0.09592 ± 0.00096			0.04207 ± 0.00042
1141	0.2051		1261	0.04218	
	0.2029			0.04165	
		0.2040 ± 0.0020			0.04192 ± 0.00042
1142	1.0170		101f	0.02852	
	1.0162			0.02875	
	1.0132			0.02916	
				0.02883	
		1.0155 ± 0.0102			0.02882 ± 0.00029

2. Determination of Nickel

Nickel was determined in a number of steel SRMs by isotope dilution mass spectrometry because significantly different concentrations had been found using other methods. The nickel was extracted as the dimethylglyoxime complex from an ammoniacal solution with chloroform and back extracted from the chloroform with a nitric acid solution. However in these solutions the concentration of ammonium salts was too large and the solution could not be analyzed by mass spectrometry. The solution was diluted and passed through a cation exchange column. The nickel was eluted with 5N nitric acid, and electrodeposited from an ammoniacal solution.

For SRM 101f, which contains about 10 percent nickel, a 2 g sample was dissolved in dilute hydrochloric acid and the solution was filtered. The insoluble residue was ignited at 500 °C and was fused with potassium pyrosulfate. The melt was dissolved in dilute hydrochloric acid and was added to the filtrate. For SRMs 1261 and 361, which contain about 2 percent nickel, a 0.5 g sample was dissolved by repeated evaporation with perchloric acid and hydrofluoric acid.

To an aliquot of the steel solution, containing approximately 2 mg nickel, a weighed portion of a standardized ^{62}Ni solution was added to produce a $^{58}Ni/^{62}Ni$ ratio of from 1.5 to 2 in the sample. The iron was oxidized with potassium persulfate and complexed with sodium citrate before the dimethylglyoxime solution was added. The solution was neutralized with ammonium hydroxide and 2 cm^3 excess added. The nickel was extracted as the dimethylglyoxime complex with chloroform and back extracted into a nitric acid solution.

The solution was evaporated to dryness and the residue dissolved in 0.1 to 0.2N nitric acid. The solution was passed through a cation column (AG50×8, 100-200 mesh). The nickel was eluted with 5N nitric acid. Two cm^3 of sulfuric acid were added to the eluate and the acids neutralized with ammonium hydroxide and 2 cm^3 excess added. The nickel was separated

by electrodeposition and taken into (2+98) nitric acid solution so that the final concentration of the nickel was 2.5 mg/cm³.

A provisional analytical procedure has been developed and used for a limited amount of isotope dilution work. Previous efforts to analyze nickel samples were frustrated by a background mass approximately 0.05 mass units above the ^{58}Ni peak. No interfering mass has been detected at any of the nickel mass positions with the present technique. The technique was patterned after the silica gel method for lead analysis (see section 4). The preparation of a nickel sample for analysis is nearly identical to the procedure used for lead, but there are major differences in the mass spectrometric heating patterns. A high purity nickel metal of natural isotopic composition was used as a working standard to evaluate the procedure.

The nickel ion currents were measured on a single stage solid sample mass spectrometer with a 6-inch radius of curvature-60° analyzer tube and a "Z" lens ion source [2]. The ion source was operated at 7.5 KV and a single filament rhenium ribbon, 0.0012 × 0.030 inch, was used. All filaments were degassed, prior to use in the mass spectrometer, in a vacuum and under a potential field to reduce the potassium and chromium background. Large ion currents of chromium and, especially, potassium were the source of major baseline interference in the nickel mass range.

The same reagents used for the lead method, silica gel and phosphoric acid, were used to mount the nickel sample on the filament. One small drop of silica gel solution was placed on the filament and dried for 5 minutes with a heat lamp and a 1 A current. One small drop, approximately 25 µg of nickel, from a nickel nitrate solution with a concentration of 2.5 mg Ni/cm³ was dried for 5 minutes by the heat lamp and a 1 A current. A small drop of 0.75N phosphoric acid was added to the filament and, with the heat lamp on, dried for 5 minutes at 1.7 A and then for 10 minutes at 2.3 A. The final product

was dark brown in color and was smooth and glassy in appearance. The sample was mounted into the spectrometer promptly because it was hygroscopic and absorbed water rapidly.

When the source pressure was approximately 1×10^{-6} torr, liquid nitrogen was added to the source coldfinger and the analysis was begun. Source pressure during an analysis was less than 3×10^{-7} torr. Each analysis was made on a strict time schedule because the $^{58}Ni/^{62}Ni$ ratio changed between 0.5 and 1 percent over the time span required to complete the ratio measurement. Failure to adhere to the time schedule, regardless of the reason, was sufficient cause to terminate the analysis.

An optical pyrometer was used to determine filament temperatures. Within the first minute of heating the temperature of the filament was adjusted to 1050 °C. This temperature was too low to yield significant ^{58}Ni ion currents and was intended to remove any potassium in the filament material, the reagents, or nickel sample. Initially, the potassium ion current was large enough to completely degrade the baseline at the ^{58}Ni position. For most samples five minutes of heating at 1050 °C reduced the potassium below the level which caused significant interference. Chromium signals were normally too small to cause significant interference.

After 5 minutes of heating the filament temperature was adjusted to 1130 °C. At this temperature the potassium was quickly reduced below the critical level that caused detectable interference and the ^{58}Ni ion current was approximately 1×10^{-12} A and decaying. The filament temperature did not stabilize in the neighborhood of 1130 °C but increased during the remainder of the analysis without any further adjustments. This unexpected response usually followed one of two general patterns. In one type the temperature increased very slowly during the next 15-20 minutes to 1150-1160 °C. The temperature remained nearly constant for approximately 10 minutes and then slowly increased to 1180-1190 °C at the end of the analysis. The ^{58}Ni signal response after the adjustment to 1130 °C was

usually a decay to the middle 10^{-13} A range before entering a growth phase that was approximately 50 minutes in duration. Occassionally, the signal remained nearly constant or decayed slightly at an intensity of $2-3\times10^{-12}$ A before continuing its growth trend. The temperature response described above was the most desirable because of a relatively slower rate of change of the $^{58}Ni/^{62}Ni$ ratio with time and because it was possible to take all data on a growing ion current.

The second type of general temperature response after the filament was adjusted to 1130 °C was a more rapid increase during the remainder of the analysis. The temperature was approximately 1180 °C after 30 minutes of heating and was significantly more than 1200 °C at the end of the analysis. The corresponding signal response was as follows: a rapid growth to a $3-5\times10^{-12}$ A intensity; a brief period of decay; and then a short growth cycle which was followed by a continuously decaying signal. The entire cycle from rapid growth to continuous decay was completed within 1/2 hour after the initial adjustment to 1130 °C. In this case all analyses were terminated and no data was obtained.

For each analysis 10 peak sets were taken between 30 and 41 minutes after the start of heating. Each peak top was monitored for 1/2 minute and magnet changes were made in discrete steps.

At the present stage of development of the nickel mass spectrometric procedure fractionation of the isotopes is the foremost problem. It was possible to routinely produce changes of several percent in the $^{58}Ni/^{62}Ni$ ratio within an analysis by simply using temperatures 20 °C higher than normal. Failure to precisely reproduce the same filament temperatures for different sample loadings was the cause of equally large differences between analyses. The full effect of the constantly changing filament temperature during an analysis has not been determined but it will be essential to hold this change to a

66

narrow limit if no means is found to stabilize the filament at some constant temperature.

The critical areas in the sample mounting procedure are the amount of silica gel on the filament and the magnitude of the drying current. Superior analytical performance was obtained when the silica gel solution dried as a thin film or as a faint spot of crystals on the filament. Filaments with large and bulky silica gel deposits yielded adequate signal intensities but the stability was poor and too erratic for a precise ratio measurement. When such filaments did yield stable signals, the rate of change of $^{58}Ni/^{62}Ni$ with respect to time was much less than normally observed.

Electrical currents of 2.3 A during the final step of the sample mounting procedure usually gave the best analytical performance. Samples dried at either a few tenths of an ampere above or below 2.3 A gave unsatisfactory analytical performance. The signal intensities were abnormal and the long term stability was not adequate for a precise ratio measurement.

When nickel samples were heated in the spectrometer, the brown glossy substance on the filament was collected on the drawing-out plate and the lower side of the source shield. This substance was sticky and moist and, at the present time, no effort has been made to determine its composition. No detrimental effect other than a minor increase in the background source pressure was detected. This substance was soluble in acetone and water. Acetone was used to spot clean the drawing-out plate after each analysis with the source mounted in the spectrometer. At the end of the day the shield and drawing-out plates were thoroughly flushed with acetone.

The results of the isotope dilution analyses are shown in Table 18. Each value for the 101f samples represents the average of 4 mass spectrometric analyses. The remaining values represent the average of duplicate analyses. The 95% analytical limit of error for a single measurement of the $^{58}Ni/^{62}Ni$ was 0.48 percent.

67

Table 18. Determination of nickel in various SRM steels.

Sample no.	Found, %	Average, %
101f-2-1	9.945	
101f-2-2	9.983	
101f-5-1	9.950	
101f-5-2	9.999	
101f-8-1	9.999	
101f-8-2	9.972	
101f-9-1	9.964	
101f-9-2	9.978	
		9.972
101e	9.485	
		9.485[a]
361-1	2.012	
361-2	2.010	
		2.011
1261-1	1.999	
1261-2	2.000	
		2.000

[a] Certified as 9.48.

D. Boron in SRM 59a, Ferrosilicon

Boron was determined in SRM 59a, Ferrosilicon, by isotope
dilution mass spectrometry. The ferrosilicon was fused with
sodium carbonate and digested in water. A weighed portion of
a standardized solution of ^{10}B was added so that the $^{11}B/^{10}B$
ratio was approximately 1. The solution was acidified with
nitric acid and the boron extracted into a chloroform -
2-ethyl-1,3-hexanediol mixture. The organic layer was washed
with water and the boron back extracted into a sodium hydroxide
solution. This layer was acidified with nitric acid and the
boron again extracted with chloroform - 2-ethyl-1,3-hexanediol
mixture, except 2 cm^3 of the chloroform - 2-ethyl-1,3-
hexanediol mixture were used instead of 20 cm^3 as used in the
first extraction. The sodium hydroxide solution, used to back

68

extract the boron, was evaporated to dryness and the residue dissolved in 2 cm^3 of water. The solution was passed through a mixed resin bed and sodium carbonate was added to the eluate so that the B/Na ratio was 2 [4].

A detailed discussion of the mass spectrometric procedure and an evaluation of the critical parameters for boron analysis are given in NBS Special Publication 260-17 [10]. A single filament tantalum-ribbon (1x30 mils) source is used. The analytical technique is the one that was devised for use with an optical pyrometer. Briefly, the temperature of the tantalum filament is adjusted in a series of steps to 750-760 °C over a 1/2 hour interval. Data are taken after 40 minutes of heating on a slowly decaying total signal intensity of $3-2\times10^{-12}$ A.

The $^{11}B/^{10}B$ ratios were determined by measuring the molecular ions $Na_2^{11}BO_2^+$ and $Na_2^{10}BO_2^+$ at masses 89 and 88 respectively. The contribution of $Na_2^{10}B^{16}O^{17}O^+$ at the mass 89 position had been experimentally evaluated by measuring the ratio $Na_2^{11}B^{16}O^{17}O/Na_2^{11}B^{16}O_2$ of a ^{11}B separated isotope solution. A value of 0.00079 was obtained for this ratio and was used to calculate the contribution from $Na_2^{10}B^{16}O^{17}O$.

The results (duplicate analyses of each sample) are shown in Table 19.

Table 19. Determination of boron in SRM 59a, Ferrosilicon.

Sample no.	Found, %
59a-1	0.0591
59a-1	0.0590
59a-2	0.0595
59a-2	0.0597
Average	0.0593

E. Uranium and Lead in Cation Exchange Bead Microstandards

Uranium has been determined on two sets of proposed microstandards and lead on one set by isotope dilution.

The first set of samples loaded with uranium and mercury in U/Hg ratios of approximately 1:10, 1:100, and 1:1000; were dried, weighed and transferred to teflon beakers. After adding a weighed aliquot of "U-235" (see section 3-A for details of the spiking procedure), about 2 cm^3 of nitric acid were added, and the solution was evaporated to 5 cm^3. The sample was fil-tered, evaporated to dryness and dissolved in 2N hydrochloric acid. The mercury was held on a strongly basic anion exchange column while the uranium was eluted. The uranium fraction was evaporated to dryness, dissolved in nitric acid (1+19), and the $^{235}U/^{233}U$ ratio determined by mass spectrometry. The uranium content was calculated from these measured ratios, the isotopic composition of the uranium in the spike and sample, the amount of spike added, and the weight of sample.

The second set of samples; loaded with uranium and lead in U/Pb ratios of approximately 1/10, 1/100, 1/1000; were spiked with both "U-235" and "Pb-206". After adding nitric acid and evaporating to about 5 cm^3 as in the first set, the solution was diluted to 20 cm^3 with water and the lead was electrolytically deposited as PbO_2. After weighing, the lead was dissolved in dilute nitric acid and hydrogen peroxide, and the solution was evaporated to dryness. The samples were dissolved in nitric acid (1+49) and the $^{206}Pb/^{208}Pb$ ratios determined by mass spectrometry. The uranium was determined in the sample solution after the electrolysis. The solution was evaporated to dryness, taken up in nitric acid (1+1) and eluted onto a strongly basic anion exchange resin. The ura-nium was removed with nitric acid (1+49). The solution was evaporated to dryness, dissolved in nitric acid (1+19) and the $^{235}U/^{238}U$ ratio determined by mass spectrometry. The lead and uranium content of the beads were calculated as done in the first set.

4. HIGH SENSITIVITY ANALYSIS

A. Silica Gel Method

1. Introduction

The precise mass spectrometric determination of the isotopic abundance ratios of samples of lead has proven to be a relatively simple process providing sufficient sample is available. Using samples, large enough to give a solution concentraion of 20 mg/cm^3 solution, it has been possible to analyze lead isotopically using the triple filament technique with a precision and accuracy of 0.02 percent [11]. Using reasonable care the blanks obtained with these large samples are usually of no consequence and, in general, corrections for the blanks are not necessary.

A completely different problem is presented however when very small samples or samples with a very small lead concentration are available. The triple filament lead procedure has not proven successful with a total lead sample of less than approximately 30-50 µg. A variety of procedures have been used by various investigators to isolate and ionize small lead samples but perhaps the easiest and most widely adopted method is to precipitate the sample as PbS which is subsequently deposited on a filament, mounted in the mass spectrometer and analyzed. This method has, however, several disadvantages. The ionization efficiency is quite low, sodium and potassium which might be present (usually from scraping the sides of the centrifuge tube in collecting the precipitate) greatly reduce or "poison" the ionization and blanks tend to be a significantly large proportion of the total sample. Akishin et al. [12] have reported that a silica-zirconia gel acted as a catalyst to produce abundant lead ions thus overcoming one of the above objections to small sample lead analysis. Cameron et al., [13] in a thorough investigation of this procedure noted that silica gel alone was as effective as the zirconia mixture and published a procedure both for the preparation of

71

the catalyst and the subsequent analysis of nanogram size samples of lead. In the procedure of Cameron et al., however, a tandem spectrometer was required and an upper limit of 0.5 μg lead was necessary to prevent an ion beam too large for the ion counting detection system in use.

We were able to duplicate the results of Cameron et al. on a similar (though not identical) spectrometer [2] using a different ion detection system [1] with very pure lead samples, SRMs 981, 982, 983. However, we noted a seemingly uncontrollable variation in ion beam size which seemed to be dependent on the amount and crystal size of the silica gel used. We also experienced some difficulty in preparing silica gel which was sufficiently free of lead to give a negligable background. The method did however seem to merit further investigation and extensive experimentation was done to carefully define the optimum conditions for precise and accurate lead analysis.

   2.   Reagents

      a.   Silica gel - Thirty grams of meta-sodium silicate ($Na_2SiO_2 \cdot 9H_2O$) was dissolved in 200 cm^3 of nitric acid solution (1+19). The nitric acid had been previously isothermally distilled from "ultra-pure" nitric acid. The solution was evaporated nearly to dryness at 160 °C ("low" setting on a hot plate). This procedure was repeated but the evaporation was carried to dryness. About 200 cm^3 of nitric acid solution (1+99) was added to the residue and the solution allowed to boil for 10 minutes. The hot solution was filtered through a medium textured filter paper. The residue was washed back into a beaker, diluted with 200 cm^3 of redistilled water, boiled for 10 minutes and allowed to cool and settle for approximately 1/2 hour. The water was carefully decanted and the washing repeated 3 or 4 more times. After the final washing and decanting the residue was diluted with 10 times its volume with redistilled water and transferred to a teflon bottle. The solution was shaken thoroughly 2 or 3 times a day for 3 days and then after a 3 hour settling time the liquid

layer was carefully decanted into a second teflon bottle.
This colloidal suspension is the "silica gel" referred to in
all subsequent operations.

      b.   <u>Phosphoric acid</u> – A phosphoric acid solution was
prepared by carefully dissolving "ultra pure grade" resublimed
phosphorous pentoxide in redistilled water in a teflon bottle
and diluting to make a solution 0.75N in phosphoric acid.

    In the preparation of all solutions only teflon ware was
used and all steps were carried out within a small Class 100
laminar flow "clean" hood.

    3.   <u>Mass Spectrometry</u>

<u>Filament preparation</u> – A single center rhenium (0.001 ×
0.030 inch) filament which had previously been degassed was
used in all cases. A small drop of the silica gel suspension
was placed on the filament and dried for 5 minutes with a heat
lamp with a current of 1 A through the filament. When dry,
only a faint spot was visible and no large particles of silica
could be seen.

    A single drop of the lead solution containing 0.1 to 1.5
µg lead in nitric acid (1+19) was placed on the filament and
dried for 5 minutes with a heat lamp and with a current of 1 A.

    A drop of the 0.75N phosphoric acid was added and dried
for 5 minutes with a heat lamp with 1.7 A current and then 10
minutes with a heat lamp and a current of 2.4 A. At the end
of the 10 minute period the filament current was carefully
raised until the entire filament was heated to a dull red
color. This normally required a current of 2.5 to 2.7 A. The
filament was then mounted in the spectrometer for analysis.

    4.   <u>Mass Spectrometric Procedure</u>

    The samples were analyzed in a 12" radius mass spectrom-
eter with an accelerating potential of 10 KV. The following
analytical procedure was used:

Time from start (minutes)	Procedure
0-1	Temperature set at 1100 °C
5	Temperature set at 1150 °C
10	Temperature set at 1200 °C
20-25	Base line scanned
30	Data taking begins. Data taken in the following pattern: 4- 208/206 ratios; 4- 207/206 ratios; 8- 204/206 ratios; 4- 207/206 ratios; and, 4- 208/206 ratios

NOTE: Decaying signals are always observed at 1200 °C. The signal decays quite rapidly at first but the rate of decay decreases at about 20 minutes to give slowly dying signals. A common lead sample of $\sim$1 µg will normally give a ^{208}Pb ion current beam current of $\sim$3×10^{-10} A.

5. Results

A series of lead standard samples (SRM 981) were analyzed and the analyses showed a precision (2 sigma) of 0.06 percent for the lead ^{208}Pb/^{206}Pb ratio, 0.03 percent for the ^{207}Pb/^{206}Pb ratio and 0.1 percent for the ^{204}Pb/^{206}Pb ratio. The method has been applied to a series of glass samples containing from 1 to 500 ppm lead in glass and to a variety of archaeological and pollution samples.

The total amount of lead loaded on a filament has been as small as 0.2 µg and undoubtedly may be reduced even further when the laboratory blank is reduced.

The method has also been used for the analysis of thalliun in glass samples containing from 0.008 to 60 ppm.

The results of these analyses are reported elsewhere in this publication.

6. Discussion

a. <u>Phosphoric acid preparation</u> - In early attempts to prepare a suitable phosphoric acid solution, commercial

reagent grade phosphoric acid was carefully purified to remove residual lead by following the purification system of Cameron et al. [13]. This procedure did, indeed, remove lead but almost always resulted in a large organic background in the spectrometer which died away very slowly. In an attempt to remove the organic material the phosphoric acid was passed through a column of carefully prepared charcoal which removed all the organic material but resulted in a lead blank higher than before. The use of "ultra pure" resublimed phosphorus pentoxide resulted in an undetectable lead blank.

       b.   <u>Silica gel preparation</u> - Silica gel prepared even with the use of "ultra pure" nitric acid always showed a small, but not negligable, lead blank. When the nitric acid was isothermally distilled the resultant silica gel gave a completely undectable lead signal.

       c.   <u>Mass spectrometry</u> - As noted by Cameron et al., [13] a small organic signal was always noted at temperatures below 1100 °C. Above 1100° however this signal decayed very rapidly and at 1285 °C was not detectable.

The use of zone refined rhenium ribbon as filament material nearly always resulted in more stable signals.

5. ATOMIC WEIGHT RESEARCH

A paper describing the measurement of the absolute isotope abundance ratio and atomic weight of rubidium was published [7]. A preliminary investigation into a high precision - high accuracy method for the determination of potassium was initiated. This method, patterned after that used for rubidium, is based on the purification of potassium chloride by crystallization as the perchlorate followed by thermal conversion to the chloride. Solutions of this purified potassium chloride are then assayed by conversion of weighed portions to potassium perchlorate.

6. SPARK SOURCE MASS SPECTROGRAPH

A. Instrumentation

1. Introduction

The spark source instrument was transferred this year from the Spectrochemical Analysis Section into the Analytical Mass Spectrometry Section. Description of the equipment and the type of work that has been performed with the spark source can be found in the yearly progress reports of the former section [14,15,16,17,18]. In recent years techniques suitable for isotope dilution analysis with the spark source mass spectrograph (SSMS) have been developed in order to provide ppm level analysis on a number of Standard Reference Materials. In this work R. Alvarez, who is still in the Spectrochemical Analysis Section, has provided the preconcentration, separation and spiking competence for these joint efforts. Description of his work on the SSMS isotope dilution analysis is included in both Section's report in order to give a complete picture of the work.

2. Ion Beam Deflector

Beam chopping has been shown [19] to be an effective means of improving precision for high level impurities by increasing the volume of sample consumed on short exposures. Deflecting electrodes, controlled by a pulse generator of variable width and frequency, allow passage of a fraction of the ions being generated in the r.f. high voltage spark. Such a system allows a wide range of exposures to be made each using approximately the same sample volume. In addition the r.f. spark frequency and duration, which normally must be varied to cover the wide dynamic range of exposure levels used, can be held constant with a beam chopper, thus maintaining identical sparking conditions for all exposures.

As a start toward development of a beam chopping system, ion beam deflecting electrodes have been built for our instrument. A photograph of the electrodes is shown in figure 5.
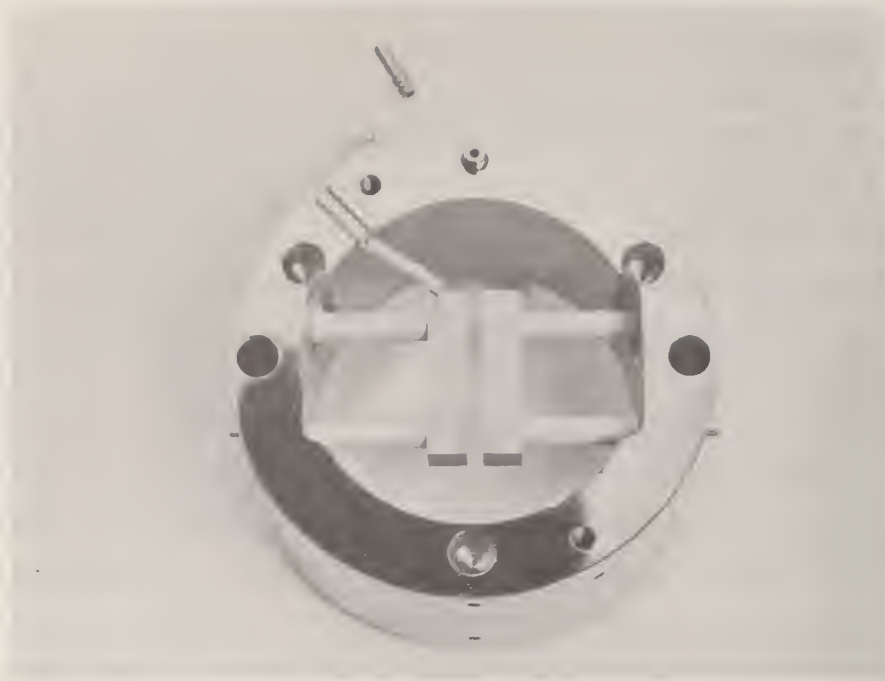
Figure 5. Beam Deflector Mounted in Source Conversion Ring.

They are mounted in a conversion ring added to the source when
it was switched from 15 KV to 24 KV operation. These elec-
trodes are symmetrical about the instrument "optical axis"
and are located approximately one half inch behind the final
defining slit in the source. Deflection of the ion beam
occurs perpendicular to the z axis of the instrument (i.e.,
the electrodes are parallel to the final defining slit). A
test pair of deflecting electrodes was made 0.25 inch square
by 1 inch long with a 0.25 inch gap between electrodes. The
dotted line in figure 6 shows the ion beam current as a func-
tion of deflecting voltage. The ion beam current was dropped
by more than a factor of 10^5 by using either -600 V or +800 V
for deflection. Since these voltages are somewhat high to use
conveniently, the gap between electrodes was reduced to 0.125
inch by replacing the 0.25 inch square electrodes with 0.3125
inch square by 1 inch long electrodes. The solid line in

figure 6 shows the ion current vs deflector voltage for the
0.125 inch gap. A negative 400 V will obviously be adequate
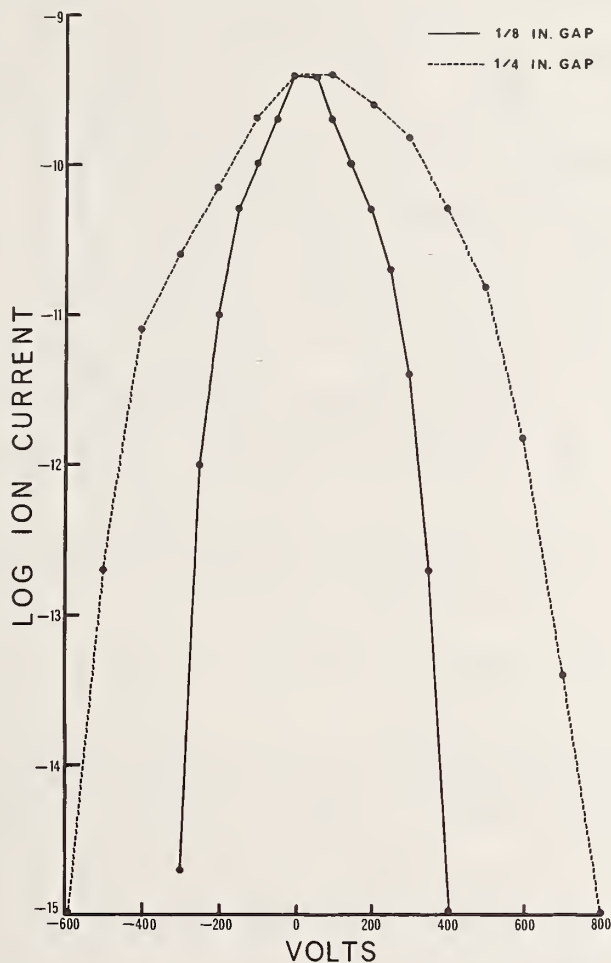to turn off the ion beam current.

Figure 6. Ion Beam Current vs Deflection Voltage.

The 20 μs ion pulses generated by our instrument would
require rise times of 10 ns or less for the beam chopper
deflecting voltage in order to effectively "chop" individual
pulses. Since this short rise time could be difficult to
obtain, the tentative plans are to synchronize the chopper
with the r.f. spark and to pass the entire pulse of ions
generated by an individual spark. The deflector plate voltage
could then be switched in the millisecond range time interval
between pulses with no difficulty.

79

3. Internal Source Baking

Hydrocarbon interferences in an analysis can normally be minimized thru baking of the source vacuum chamber and by pre-sparking of the surface of the sample. A source chamber bake, to be effective, must last several hours since the sample electrodes and some source parts are insulated electrically, and therefore thermally, from the vacuum chamber. Presparking lowers hydrocarbons thru physical removal of the contaminants on the sample surface and also thru heating of sample and internal source parts. On occasion, hydrocarbon interferences have caused some difficulty with our isotope dilution analysis on the SSMS. Since isotope dilution samples are either plated or evaporated onto the surfaces of a pair of high purity (69 grade) gold electrodes, presparking cannot be used as it would remove the sample itself. Long baking of the source vacuum chamber is not practical when relatively fast sample thruput is desired.

An electron bombardment system is being tested as a means of baking the sample internally. A 0.030 by 0.001 inch tantalum ribbon was mounted in the space between the final defining slit and the second aperture (both at ground potential). Electrical feedthrus are located on a flange once used for an ion gauge. A power supply for the bakeout unit provides:

1) 0-10 V ac power from a filament transformer
2) 0 to -300 V filament bias
3) an emission current meter
4) 0-1 ma meter in the 24 KV ion accelerator power supply (at ground potential).

With the ion accelerator on, electrons are drawn thru the second aperture at ground potential to the first aperture plate at 24 KV. Some of the electrons pass on thru the first aperture to the sample electrodes also at 24 KV. A test of this system gave a maximum heater current of 3.3 A ac. A maximum of 15 ma emission current and 0.4 ma ion accelerator current was obtained when the bias voltage was -70 V. This

provides 33 watts IR heating and 5 watts electron bombardment heating to the region of the final defining slit and second aperture, and 10 watts of heating to the first aperture and sample from the ion accelerator current.

A test sample using this system showed a significant pressure rise during baking with a subsequent decrease in the hydrocarbon content in SSMS spectra as compared to the unbaked sample. A mass spectrum recorded during baking (ionization was by electron bombardment and not by the r.f. spark) gave major peaks at masses 16, 17, 18, 19, 28 and 44, however the ion current was only in the 10^{-15} A range. A different filament transformer appears necessary in order to improve electron emission so that higher currents to the 24 KV aperture can be obtained.

Commercial bakeout units similar to this one have been produced; however due to various modifications made to our instrument it was simpler to build a unit than to adapt a commercial unit.

B. Analysis of Materials by Direct Sparking With SSMS

As in previous years a number of materials were examined directly with the SSMS. Most of the samples were Standard Reference Materials and of relative high purity. Some of the samples run were high purity silver, cadmium and molybdenum metals, and compounds such as thallium chloride, potassium dichromate and arsenic trioxide. In none of these analyses were any standards available containing known impurity levels in the same matrices; therefore only estimated concentration levels could be reported. For silver, cadmium and molybdenum however, residual resistivity ratios (RRR) measurements were used to select samples containing the lowest and highest (electrically active) impurity levels. The relative concentration reported by SSMS then gave an indication of which impurities were controlling the observed RRR.

81

Acceptance testing was performed on a series of new SRM steel samples being produced mainly for emission spectrometry use. Test samples from the various heats of SRMs 1261 thru 1264 were examined by a number of different techniques, with the SSMS reporting on 13 to 15 elements. The available SRMs ingot irons, used as standards, were certified for only a few of the elements assigned to the SSMS for analysis. Some of the other elements were compared to values reported by other techniques on the test sample of SRM 1261 and the remainder were computed from estimated sensitivity factors.

Due to a number of factors the 1264 steel was remade with some changes in element concentrations. The acceptance testing of the new sample (1264 heat #2) by SSMS was based on a comparison to the first sample (1264 heat #1) and to SRM 1261 on which actual analysis values for certification were then becoming available. The results of these analysis are given in Table 20. The results are based on a 1, 3, 10, 30, etc., set of graded exposures and therefore only about three exposures each were measurable on the "standard" and "unknown". The first column gives the ratio of the amount of an element found in heat #1 to that found in heat #2. The values in the second column are ppm by weight in heat #2 of 1264 computed using the preliminary analysis values assigned to the first heat. Some of the values used from the first heat are based on known standards (one or more steps removed) and others are from estimated sensitivity factors. The last column gives an analysis of the second heat based on a direct comparison to SRM 1261. All values for 1261 except for lanthanum are considered reliable. The agreement on the 1264 heat #2 analysis using the two different samples as standards is good considering the use of estimated sensitivity factors in the original analysis of the heat #1 sample. The factor of 2 agreement between the lead values is reasonable considering that the lead concentrations in the samples used as "standards" differed by a factor of approximately 600. Similar differences in

82

concentration between the two "standards" also existed for
bismuth (40/1), antimony (10/1) and silver (20/1).

Table 20.   Spark source mass spectrographic analysis of SRM 1264,
Low Alloy Steel (0.9 C) (heat #2).

	Ratio of $\dfrac{1264 \text{ heat } \#2}{1264 \text{ heat } \#1}$	ppm wt vs 1264 heat #1	ppm wt vs 1261
Bi	0.06	13	20
Pb	1.6	200	400
Hf	>20	50	---
Pr	0.18	0.7	---
Ce	0.15	5	5
La	0.12	1	2 to 5
Te	0.03	1	2
Sb	1	300	200
Sn	0.07	20	---
Ag	0.003	0.2	0.2
Se	0.15	2	3
Ge	1.4	30	---
Zn	0.01	0.4	---

C.   Analysis by Isotope Dilution

1.   Introduction

The Spark Source Mass Spectrograph has two characteristics
important to isotope dilution:

a)   With the high voltage r.f. spark used on the SSMS
all elements, regardless of ionization potential, can give a
just detectable signal with from 10^{-10} to 10^{-11} g of material.
(Considerably more is actually required to obtain reliable
measurements of istotopic ratios.)

b)   The photographic plate covers the mass range from 7
to 240; thus all elements are detected simultaneously. It is
therefore possible to simultaneously determine many elements
of diverse ionization potentials from a single sample loading

with sensitivities below 1 ppm. The multi-element capability of the SSMS enables efficient use of time on the chemistry and the SSMS; however it also enables the use of relatively simple group separation techniques which in turn tend to hold down blank problems.

Based on previous experience we would consider it feasible to attempt analysis by SSMS isotope dilution if 0.1 µg (1×10^{-7} g) or more of a spiked element could be loaded into the SSMS for sparking.

The photographic plate detection system presently used imposes a ±5 percent precision on the results of an isotope dilution analysis. This does not compare favorably with better than 0.1 percent precision possible with thermal ion source mass spectrometers; however the work with SSMS supplements thermal ion work and does not attempt to compete with it. Analysis for elements at the ppm level which would be impossible to perform with thermal ion units can be done with SSMS isotope dilution techniques. The work in general has only been applied to elements and concentration levels where other more precise techniques cannot be used.

In last year's annual report [18], a stable isotope dilution-spark source mass spectrographic method was outlined (ID-SSMS) for analyzing ingot iron. Silver, copper, molybdenum and nickel were simultaneously determined in the 100-mg samples of SRM 1165 using a chemical preconcentration step to separate the spiked analytes from the matrix. The concentrations ranged from 0.0005 percent for silver to 0.025 percent for nickel. Cobalt, a mononuclidic element, was also determined at the same time by adding known amounts of cobalt to half of the samples used for the isotope dilution determinations and measuring the $^{59}Co/^{60}Ni$ and $^{59}Co/^{58}Ni$ ratios. Details of the method including a comparison of the results obtained with the certified values was published recently in Analytical Chemistry [20].

84

2. Materials Analyzed

a. Steel standard reference materials - The preceding method [18,20] was applied to the analysis of SRM 1265, Electrolytic Iron, intended as a renewal standard reference material. The procedure was altered somewhat in order to investigate whether other elements could also be separated and thus determined. Titanium was of particular interest. After extracting the iron into the organic phase, the aqueous phase was evaporated to a few tenths of a cm^3 instead of being electrolyzed as in the published procedure. The residue was transferred to high purity gold wires and ignited at 450 °C for 20 minutes in a tube furnace equipped with a quartz tube liner. The wires were then sparked in the mass spectrograph and the spectrum was photographically recorded. A line corresponding to SO^+, which is an ion fragment from the sulfate in the residue, interfered with an intensity measurement of the line produced by the ^{48}Ti. The sulfate in combination with alkali cations is not removed by ignition. Some of the sulfate came from the ^{47}Ti spike solution, since sulfuric acid had been used to dissolve the enriched isotope material. Moreover, during the subsequent dilutions of the 1 mg/cm^3 ^{47}Ti stock solution, to prevent hydrolysis, the acid strength had been maintained with sulfuric acid. Had the production of SO^+ with this procedure been anticipated, these dilutions could have been performed with perchloric acid. Because of interferences of this type and those from combinations of anions and cations, it was preferred to incorporate an electrodeposition step in the previous analytical procedures that had been developed. This has the advantage of providing the isotopically altered analytes relatively free of other anions and extraneous cations thus greatly simplifying the photographically recorded spectrum.

Although titanium was not determined, other spiked analytes yielded interference-free lines on the emulsion. The results for these elements are given in Table 21.

85

Table 21. Spark source mass spectrographic isotope dilution analysis of SRM 1265, Electrolytic Iron.

Element	Average concentration percent by weight	95% Confidence limits	Number of determinations
Cu	0.0058	0.0003	8
Cr	0.0075	0.0002	9
Ni	0.040	0.001	9
Mo	0.0041	0.0005	6

In the analytical procedure, most of the iron and some of the molybdenum is extracted with methyl isobutyl ketone (MIBK) and if the molybdenum present in the sample and the molybdenum spike were not in equilibrium, erroneous results would be obtained. This attainment of equilibrium, an essential condition of the method, is usually ensured by cycling analytes and spikes through oxidation-reduction states. However, in attempting to determine several trace elements simultaneously, indiscriminate use of reagents, other than those of highest purity, would prohibitively increase the method blank for common elements thus precluding their determination.

Because of the several stable valence states that molybdenum possesses, one tends to be even more concerned regarding the attainment of equilibrium between that analyte and its spike. Consequently two additional experiments were run in which the spiked samples were dissolved as before in hydrochloric acid but then evaporated to dryness and treated with concentrated nitric acid. Individual results of 0.0039 percent and 0.0042 percent were obtained. It was concluded from this that equilibrium of the molybdenum oxidation states was not causing difficulty in the analysis.

In another series of experiments designed to determine titanium, the isotopically altered trace elements were electrodeposited at a current density lower than usually employed. Although under these conditions, titanium was electrodeposited

as was evident from the mass spectrum, it could not be determined because of interference from the doubly charged ^{96}Mo on the singly charged ^{48}Ti. The relative amount of molybdenum compared to titanium on the gold wires was greater in this case than in the evaporation procedure. This interference from the doubly charged ^{96}Mo was eliminated by extracting the solution with MIBK before electrolysis. Obviously with this extraction step, molybdenum would be replacing titanium as an analyte.

Thus none of the procedures attempted permitted both molybdenum and titanium to be determined simultaneously from the samples already spiked and available. Therefore titanium was not determined since it would require twice as much work, and another technique was already providing results on titanium.

An ID-SSMS method was developed for determining a number of chemically diverse elements in low-alloy steel. Copper, silver, cerium, neodymium, selenium, tellurium and zirconium ranging from 0.040 percent for copper to 0.00031 percent for neodymium were determined in a steel material subsequently issued as SRM 1261, Electrolytic Iron. The procedure will be detailed in a manuscript being prepared for publication.

      b. <u>Botanical materials (Orchard Leaves)</u> - This is the first of a series of plant standard reference materials being issued to calibrate analytical procedures. A number of trace elements, essential to plants, are being determined by ID-SSMS. In addition, the method yields upper concentration limits for a number of elements. Of particular significance is the presence of an abnormally high concentration of lead.

      c. <u>High-purity reagents</u> - The purity of reagents is fundamental to reliable trace element determinations by most analytical methods. Samples of high-purity perchloric acid were analyzed by an ID-SSMS procedure to determine their suitability as reagents for high-purity materials. Approximately 50 cm^3 of each sample were spiked with enriched isotope

solutions of fourteen elements of interest. An aliquot of
the spiked solution was evaporated to a small volume and
transferred to a pair of high-purity gold wires. The wires
were then ignited in a tube furnace to remove hydrocarbons
and residual perchloric acid. The mass spectra were photo-
graphically recorded and the results were calculated from the
measured isotope ratios, and the other experimental data. The
results for two lots of perchloric acid are listed in Table 22.

Table 22. Analysis of high-purity perchloric acid by isotope dilution
— spark source mass spectrography.

| | Concentrations in parts per billion (ng/g) | |
	Lot "A"	Lot "B"
Ag	< 0.5	< 0.5
Ca	40	7
Cd	2	4
Cr	22	18
Cu	2	3
Fe	15	10
Mg	14	4
K	7	9
Ni	4	< 0.5
Pb	14	16
Sn	< 2	< 1
Zn	22	17
Ba	< 10	10
Ti	3	2

All fourteen impurity elements were determined simulta-
neously. In this method, if the enriched isotope spikes and
impurity elements are in physical and chemical equilibrium,
possible losses that may occur during the preconcentration and
handling steps do not affect the final results. This should
be true for these elements under these experimental conditions.
Moreover, providing that enough material is recovered to detect
the "spiking" isotope, either an actual concentration or upper
limit can be reported.

3. Standard Reference Materials for the Spark Source
    Mass Spectrograph

NBS has produced one Standard Reference Material specifi-
cally for SSMS use. This is SRM 685 a high purity gold sample.
In addition there are several SRM samples not produced for
just the SSMS but having impurity levels ideal for SSMS needs.
These are: (a) a high purity platinum sample, SRM 680, and a
companion sample of platinum doped with 12 elements in the 0.5
to 12 ppm level, SRM 681; (b) two zinc samples in shot and
bar form, SRMs 728 and 683, of the same composition with 7
impurities determined from 20 ppb to 11 ppm. To date response
to these SRM samples has been modest.

Based on formal and informal discussions of standards at
SSMS users meetings and on the results of a survey on standards
taken for one of these meetings it is apparent that standards
requirements cover almost all conceivable types of matrices.
Since the needs are so widespread there does not appear to be
any one matrix which is of interest to a sufficient number of
laboratories to justify its production as a standard for SSMS
needs alone.

For the forementioned reasons NBS is not presently engaged
in producing standards specific for SSMS needs. This would be
changed if there was sufficient interest shown in a given
matrix in the future. There are a number of materials, however,
being produced for other uses which will meet some of the needs
of the SSMS. The gold, platinum and zinc SRMs mentioned are
available now and the series of iron SRMs and orchard leaf
samples are in the process of being certified. In addition a
series of Trace Elements in Glass (TEG) samples now being
certified could be useful for glass and possibly rock analysis.
These samples have been doped with 61 elements at the 500, 50,
1 and 0.02 ppm level. About one third of the elements are
being certified.

7. MISCELLANEOUS

A. Oxidimetric Standard Reference Materials

1. SRM 136c, Potassium Dichromate

The replacement for SRM 136b, Potassium Dichromate oxidimetric standard to be designated SRM 136c, was submitted for the determination of homogeneity and effective purity. The effective purity was also determined coulometrically by George Marinenko of Section 310.03.

Twenty drums of 25 lb each of potassium dichromate were received and after mixing, a representative sample of approximately 50 g was removed from each drum. Four composite samples were prepared by mixing 10 g of material from 5 of the representative samples of potassium dichromate for each composite.

For the determination of homogeneity of the potassium dichromate, each of the 20 representative samples was run and 12 were repeated. Ferrous ammonium sulfate, hexahydrate was used for the comparison between samples. All values fell within ±0.01 percent of the mean except Nos. 8 and 17 but on repeat runs they were also within these limits (Table 23).

At the same time the homogeneity determinations were made SRM 136c was compared to SRM 136b. The effective purity of SRM 136b is 99.978 percent. The effective purity of SRM 136c was found to be 0.011 percent higher than SRM 136b using the homogeneity runs (Table 23) and 0.009 percent higher than SRM 136b using the composite sample runs (Table 24) for an average of 0.010 percent higher than SRM 136b. The effective purity of SRM 136c would be 99.988 percent when compared with SRM 136b.

Table 23. Homogeneity of SRM 136c, Potassium Dichromate using ferrous ammonium sulfate, hexahydrate.

Date	Bottle no.	SRM 136c g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ per g $K_2Cr_2O_7$	SRM 136b g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ per g $K_2Cr_2O_7$
9/15	1	8.01025	8.00960
	3	8.01003	8.00969
	5	8.01056	8.00928
	7	8.01002	
	9	8.01048	
	11	8.01013	
	13	8.00991	
	15	8.01004	
9/17	17	8.00784[a]	8.00896
	19	8.00935	8.00906
	2	8.00962	
	4	8.00992	
	6	8.00951	
	8	8.00423[a]	
	10	8.00964	
	12	8.00948	
	14	8.00918	
9/19	16	8.00909	8.00844
	18	8.00944	8.00858
	20	8.00910	
	4[b]	8.00956	
	5[b]	8.00924	
	8[b]	8.00962	
	17[b]	8.00941	
10/13	1[b]	8.00951	8.00892
	8[b]	8.00965	8.00877
	9[b]	8.00947	8.00878
	17[b]	8.00961	
10/16	3[b]	8.00983	8.00883
	7[b]	8.00998	8.00895
	11[b]	8.00985	8.00867
	13[b]	8.00983	
	15[b]	8.00970	
	Average	8.00971	8.00896
	s.d.	$\pm$ 0.00037 (0.005%)	$\pm$ 0.00037 (0.005%)

[a] Omitted from average.

[b] Repeat runs.

Table 24. Effective purity of SRM 136c, Potassium Dichromate compared to SRM 136b, Potassium Dichromate.

Composite no.	SRM 136c g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ per g $K_2Cr_2O_7$	SRM 136b g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ per g $K_2Cr_2O_7$
I	8.00994	8.00892
II	8.01009	8.00877
III	8.00965	8.00878
IV	8.00962	
IV	8.00950	8.00883
III	8.00976	8.00895
II	8.00952	8.00867
I	8.00923	
Average	8.00966	8.00882
s.d.	± 0.00027(0.003%)	± 0.00010(0.001%)

The effective purity of SRM 136c, when compared to SRM 83c, Arsenic Trioxide (99.987%), was determined to be 99.984 percent. The results are given in Table 25. George Marinenko found 99.982 percent by coulometry. The average of the three determinations gives an effective purity for SRM 136c, Potassium Dichromate of 99.984 percent. The details of the assay will appear in NBS Special Publication 260-24 [21].

Table 25. Effective purity of SRM 136c, Potassium Dichromate
compared to SRM 83c, Arsenic Trioxide.

Composite no.	g $K_2Cr_2O_7$	g As_2O_3[a]	g $K_2Cr_2O_7$ per g As_2O_3	Effective purity (%)
I	0.990797	0.999499	0.991294	99.991
II	0.991312	0.999954	0.991358	99.985
III	0.991617	1.000361	0.991259	99.994
IV	0.991803	1.000530	0.991278	99.992
IV	0.991584	1.000158	0.991427	99.978
III	0.991270	0.999857	0.991412	99.979
II	0.991283	0.999907	0.991375	99.983
I	0.991404	0.999957	0.991447	99.976
I	0.991420	1.000036	0.991384	99.982
II	0.991455	1.000059	0.991397	99.981
III	0.991378	1.000038	0.991340	99.986
IV	0.991080	0.999653	0.991424	99.978
			Average	± 99.984
			s.d.	0.006

[a] Effective purity of SRM 83c, Arsenic Trioxide = 99.987%.

B. Intercomparison of Oxidimetric Standard Reference Materials

The intercomparison of the oxidimetric standard reference materials has been completed. A special publication [21] will be published giving the results and the details of methods for this intercomparison.

1. SRM 40h, Sodium Oxalate and SRM 83c, Arsenic Trioxide

A potassium permanganate solution was used to compare SRM 40h, Sodium Oxalate and SRM 83c, Arsenic Trioxide. The procedure for the titration of SRM 40h with potassium permanganate is given on the Certificate of Analysis (see Appendix III). The recommended procedure for the dissolution of arsenic

93

trioxide calls for sodium hydroxide and acidifying with hydro-chloric acid. Since the possibility of a side reaction of hydrochloric acid and potassium permanganate existed a study was made to eliminate hydrochloric acid from the procedure. In the modified procedure, SRM 83c was dissolved in a sodium carbonate solution and acidified with sulfuric acid. An osmium tetroxide solution and a manganous sulfate solution were used as catalysts.

SRM 40h, Sodium Oxalate was found to have an effective purity of 99.941 percent when compared to SRM 83c, Arsenic Trioxide (99.987%) Table 26.

Table 26. Effective purity of SRM 40h, Sodium Oxalate compared to SRM 83c, Arsenic Trioxide.

Composite no.	g $KMnO_4$ sol. per g $Na_2C_2O_4$	g $Na_2C_2O_4$ per g As_2O_3[a]	Effective purity (%)
I	145.1841	0.737968	99.953
II	145.1777	0.737936	99.948
III	145.1539	0.737815	99.932
IV	145.1628	0.737860	99.938
IV	145.1459	0.737774	99.926
III	145.1624	0.737858	99.938
II	145.1695	0.737894	99.943
I	145.1598	0.737845	99.935
I	145.1730	0.737912	99.945
II	145.1718	0.737906	99.944
III	145.1715	0.737904	99.944
IV	145.1694	0.737893	99.942
		Average	99.941
		s.d.	$\pm$ 0.007(0.007%)

[a] g $KMnO_4$ per g As_2O_3 = 196.735.

94

2. SRM 40h, Sodium Oxalate and SRM 136c, Potassium Dichromate

Sodium oxalate and potassium dichromate can not be compared directly. Sodium oxalate and ferrous ammonium sulfate were titrated with a potassium permanganate solution and then the potassium dichromate was compared with the ferrous ammonium sulfate. The ratios of SRM 136c to the ferrous ammonium sulfate is given in Table 27, the ratio of SRM 136c to potassium permanganate solution in Table 28, the ratios of SRM 136c and SRM 40h in Table 29 along with the effective purity of SRM 40h. The effective purity of SRM 40h was found to be 99.967 percent when compared to SRM 136c.

Table 27. SRM 136c, Potassium Dichromate compared to ferrous ammonium sulfate, hexahydrate.

Composite no.	g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ per g $K_2Cr_2O_7$
I	8.01026
II	8.01025
III	8.00965
IV	8.00948
IV	8.00965
III	8.00994
II	8.00961
I	8.00911
I	8.00965
II	8.00971
III	8.00996
IV	8.00995
Average	8.00975
s.d.	$\pm$ 0.00032 (0.004%)

95

Table 28. SRM 136c, Potassium Dichromate compared to
potassium permanganate solution.

g $KMnO_4$ sol. per g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	g $KMnO_4$ sol. per g $K_2Cr_2O_7$[a]
26.2957	210.6220[b]
26.2904	210.5795
26.2885	210.5643
26.2898	210.5747
26.2842	210.5299
26.2869	210.5519
26.2856	210.5411
26.2862	210.5459
26.2879	210.5595
26.2887	210.5659
26.2889	210.5675
26.2885	210.5643
Average	210.5586
s.d.	$\pm$ 0.0149(0.007%)

[a] 1 g $K_2Cr_2O_7 = 8.00975$ g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (Table 7).

[b] Omitted from average.

Table 29. Effective purity of SRM 40h, Sodium Oxalate compared to SRM 136c, Potassium Dichromate.

Composite no.	g $KMnO_4$ sol. per g $Na_2C_2O_4$	g $Na_2C_2O_4$ per g $K_2Cr_2O_4$ [a,b]	Effective purity (%)
I	153.8730	1.36839	99.841 [c]
II	154.0710	1.36663	99.970
III	154.0741	1.36661	99.971
IV	154.0513	1.36681	99.956
IV	154.0492	1.36682	99.956
III	154.0679	1.36666	99.967
II	154.0646	1.36669	99.965
I	154.0953	1.36642	99.985
I	154.0486	1.36683	99.955
II	154.0395	1.36691	99.949
III	154.0902	1.36646	99.982
IV	154.0470	1.36685	99.954
IV	154.0623	1.36671	99.964
III	154.0787	1.36657	99.974
II	154.0896	1.36647	99.981
I	154.0743	1.36660	99.972
		Average	99.967
		s.d.	± 0.011(0.011%)

[a] 1 g $K_2Cr_2O_7$ = 210.5586 g $KMnO_4$ sol. (Table 8).

[b] Effective purity SRM 136c, Potassium Dichromate = 99.983%.

[c] Omitted from average.

C. Archaeological Samples

As for the past several years the cooperative program with Dr. Robert H. Brill, Curator, Corning Museum of Glass has been continued. This program is aimed towards determining the suitability of using precision lead isotopic analyses for the dating and/or tracing of objects of archaeological interest.

Some examples of the various parts of this program are: a series of samples of lead extracted from bronze vessels from Sardinia were examined. Sardinia has been proposed as the source of lead in some Etruscan bronzes. Also examined were a series of ancient Egyptian kohls (mostly finely powdered galena) dating from 2200 B.C. to 1300 B.C. These give an idea of the kinds of galena ore actually in use in Egypt at that time. For this same use samples of lead pigs from the British Museum known to have been from English lead mines were analyzed. Also analyzed were a set of samples from ancient coins as well as ore samples from the same areas and a variety of other objects.

As an extension of the above cooperative effort a number of additional samples have been examined where it was hoped that the high precision lead analyses would help in determining the authenticity of art objects held in the collections of public museums. Again, as examples, samples from the "Etruscan Horse" held by the Metropolitan Museum of New York and of a smaller horse of known origin have been analyzed. The analyses of lead pigment samples from a large variety of paintings of known origin have also been completed. Dr. Brill is serving as coordinator for these various programs.

D. Air Pollution Analyses

The assay of the lead content of a series of air sample filters taken from Boston and Hilo, Hawaii has been completed. As might be expected those taken in Boston contained a relatively large amount of lead ($\sim$50 μg) and the analyses presented

no particular challenge. The filters collected from Hawaii however (through which about four times the volume of air had passed) contained a much smaller quantity (∿2-4 µg) of lead. The successful analysis of the lead content of these was completed utilizing the small sample plating technique for separation and the silica gel technique for the isotopic measurements. Both of these methods are described in detail in earlier sections.

This preliminary work was done in anticipation of receiving for analysis a series of air sample filters to be taken this fall on an Antartic Expedition. The Antartic filters are expected to contain even smaller quantities of lead in the order of 0.2 to 1 µg.

It is hoped these analyses will contribute to an understanding of the global distribution of air polluting materials and ultimately, to the control of these materials.

8. ACKNOWLEDGMENTS

9. PERSONNEL AND ACTIVITIES

A. Personnel Listing

William R. Shields, Section Chief

Joy J. Shoemaker, Secretary

Mass Spectrometry (absolute isotope ratio) --

Ernest L. Garner

Mass Spectrometry (isotope dilution) --

Larry J. Moore

Mass Spectrometry (nuclear materials) --

I. Lynus Barnes

Stoichiometry --

Thomas J. Murphy

Stoichiometry (nuclear materials) --

Lawrence A. Machlan

Separation and Purification --

Keith M. Sappenfield

Design and Fabrication --

William A. Bowman, III

Spark Source Mass Spectrometry --

Paul J. Paulsen

Charles W. Mueller

B. Publications

1. Analytical Mass Spectrometry Section: Summary of Activities July 1968 to June 1969, NBS Technical Note 506, Ed. W. R. Shields, (1970).

2. P. J. Paulsen, R. Alvarez and C. W. Mueller, "Spark Source Mass Spectrographic Analysis of Ingot Iron for Silver, Copper, Molybdenum, and Nickel by Isotope Dilution and for Cobalt by an Internal Standard Technique", Anal. Chem., 42, 673-675 (1970).

C. Talks

1. I. L. Barnes, K. M. Sappenfield and W. R. Shields, "The Mass Spectrometric Analysis of Sub-Picogram Quantities

of Lead", International Conference on Mass Spectroscopy in Kyoto, Japan, September, 1969.

2. P. J. Paulsen, R. Alvarez and C. W. Meuller, "Determination of Trace Elements in Iron Using Isotope Dilution-Spark Source Mass Spectrometry", 8th National Meeting of the Society for Applied Spectroscopy, Anaheim, California, October, 1969.

3. I. L. Barnes, K. M. Sappenfield, T. J. Murphy and W. R. Shields, "The Mass Spectrometric Analysis of Subpicogram Quantities of Lead", Eastern Analytical Symposium, Inc. Session of Microanalytical Standards, New York City, November, 1969.

4. W. R. Shields, "Fabrication and Use of Ultra-High Vacuum Systems for Mass Spectrometry", American Vacuum Society Meeting, NBS, December, 1969.

5. R. H. Brill, W. R. Shields and J. M. Wampler, Seminar: "Application of Science in the Examination of Works of Art", Museum of Fine Arts, Boston, June, 1970.

D. Committee Activities

L. A. Machlan

Member, Chemistry Panel of Interagency Board of Civil Service
    Examiners
Member, ANSI Standards Committee N101

T. J. Murphy

Member, Chemistry Panel of Interagency Board of Civil Service
    Examiners
Member, Meeting Arrangements Committee, Chemical Society of
    Washington
Member, Committee on Annual Report of Atomic Weights,
    American Chemical Society
Manager, Chemical Society of Washington
Member, Committee on Analytical Reagents of the American
    Chemical Society

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U. S. Department of Commerce
Maurice H. Stans
Secretary

National Bureau of Standards
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APPENDIX I

Certificate of Analysis

Standard Reference Material 984
Rubidium Chloride

RbCl, rubidium assay, weight percent...99.90 ± 0.02

Absolute abundance ratio, $^{85}Rb/^{87}Rb$...2.593 ± 0.002

This lot of rubidium chloride was prepared to ensure material of intermediate purity and high homogeneity. The material is somewhat hygroscopic, absorbing approximately 0.6 percent moisture in a 75 percent relative humidity at room temperature, but can be dried to the original weight by desiccation over freshly exposed P_2O_5 or $Mg(ClO_4)_2$ for twenty-four hours. The material should therefore be stored with a desiccant such as P_2O_5.

The assay of this material is based on the determination of rubidium by a combination of gravimetry and isotope dilution analysis on eight samples of about 2 g each of the dried RbCl. More than 99% of the rubidium was precipitated, filtered and weighed as rubidium perchlorate. The weight of $RbClO_4$ was corrected for potassium and cesium perchlorate. The soluble rubidium was determined by isotope dilution mass spectrometry. The total rubidium was the sum of the rubidium from the rubidium perchlorate and the rubidium from the filtrate. All weighings were corrected to vacuum and the atomic weights used in the calculations were from the 1969 Table of Atomic Weights. The indicated tolerance is at least as large as the 95% confidence level for a single determination.

Chloride was determined by silver coulometry to be 29.32 weight percent. Preferential oxidation of iodide and bromide showed that the material contains <0.001% I and <0.003% Br. Flame emission spectrometry indicated lithium, <0.02 ppm; sodium, 2.3 ppm, potassium, 420 ppm; and cesium 24 ppm. Emission spectrographic examination indicated, in addition, calcium, <10 ppm; magnesium, <10 ppm; silicon, <10 ppm; and aluminum, detection questionable. The loss on ignition at 500 °C (20 hours) was 0.010% and the insoluble matter was 0.0001%. A materials balance shows that 99.99 ± 0.02 weight percent of the material is accounted for.

The absolute abundance ratio of ^{85}Rb/^{87}Rb was determined by triple-filament solid-sample mass spectrometry. Mixtures of known ^{85}Rb/^{87}Rb ratio, prepared from nearly isotopically pure separated rubidium isotopes, were used to calibrate the mass spectrometers. The indicated uncertainties are overall limits of error based on 95 percent confidence limits for the mean and allowances for the effects of known sources of possible systematic error. Details of the preparation and measurements are described in a published paper [J Res NBS, 73A, 511-516 (1969)].

The following members of the Analytical Chemistry Division contributed to the characterization of this material: T. J. Murphy and P. J. Paulsen - rubidium assay; G. Marinenko - chloride assay; T. C. Rains and T. A. Rush - flame emission determinations; E. K. Hubbard - emission spectrographic analysis; and E. J. Catanzaro and E. L. Garner - absolute ratio determination.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of W. R. Shields.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by J. L. Hague.

Washington, D. C. 20234   J. Paul Cali, Acting Chief
July 27, 1970   Office of Standard Reference Materials

106

U. S. Department of Commerce
Maurice H. Stans
Secretary

National Bureau of Standards
L. M. Branscomb, Director

APPENDIX II

Certificate of Analysis

STANDARD REFERENCE MATERIAL 136c

Potassium Dichromate

(Oxidimetric Standard)

Purity on basis of effective oxidizing power . . . . 99.98 ± 0.02 percent

This lot of material was prepared to ensure material of high purity and uniformity. It conforms to the American Chemical Society specification for analytical reagent grade material, but is not to be considered as entirely free from traces of impurities. It is certified only for its effective oxidizing power.

Standardizations have been made by the coulometric method by G. Marinenko (see NBS J. Res. 67A, 453 (1963)), by direct comparison with arsenic trioxide SRM 83c, and by comparison with the previous SRM 136b through ferrous ammonium sulfate by K. Sappenfield. Impurity tests to the ACS specifications were made by W. P. Schmidt, emission spectrography by V. Stewart, and spark-source mass spectrography by C. W. Mueller.

Drying tests indicate that losses of the order of 0.005 percent are obtained on a few hours drying at 105 °C; long time drying indicates that losses approach 0.01 percent. The problem of occluded and surface moisture will be studied before a final certificate is issued. The effective assay is based on the sample as issued. The tolerance indicated is at least as large as the 95 percent confidence limits for a single determination, and include terms for inhomogeneities in the material as well as analytical error.

The overall direction and technical measurements leading to certification were performed under the chairmanship of R. A. Durst.

The technical and support aspects in the preparation, certification, and issuance of this standard reference material were coordinated through the Office of Standard Reference Materials by J. L. Hague.

Washington, D. C. 20234
March 24, 1970

J. Paul Cali, Acting Chief
Office of Standard Reference Materials

107

U. S. Department of Commerce
Maurice H. Stans
Secretary

National Bureau of Standards
A. V. Astin, Director

Certificate of Analysis

Standard Reference Material 40h
Sodium Oxalate

$Na_2C_2O_4$, effective purity ....99.95 ± 0.05 percent

This lot of sodium oxalate was prepared to ensure material of purity and uniformity compatible with its use as a working standard for oxidation-reduction reactions. The material conforms to the American Chemical Society specification for reagent-grade material, but should not be considered as entirely free from impurities such as moisture, sodium hydrogen oxalate (0.03%), and sodium hydrogen carbonate (0.03%). The material is not appreciably hygroscopic.

The effective purity of the sodium oxalate can be realized in the standardization of $KMnO_4$ solutions by use of the directions on this certificate. Homogeneity testing, effective purity, sodium hydrogen oxalate and sodium hydrogen carbonate determinations were made by K. M. Sappenfield; American Chemical Society specification tests were made by W. P. Schmidt of the Analytical Chemistry Division.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of W. R. Shields.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by J. L. Hague.

Washington, D. C. 20234
April 24, 1969

W. Wayne Meinke, Chief
Office of Standard Reference Materials

Standardization of 0.1N permanganate. Transfer 0.3 g of sodium oxalate (dried at 105 °C) to a 600-ml beaker. Add 250 ml of diluted sulfuric acid (5+95) previously boiled for 10 to 15 minutes and then cooled to 27 ± 3 °C. Stir until the oxalate has dissolved. Add 39 to 40 ml (0.3 g of sodium oxalate requires approximately 44.8 ml of $0.1N$ $KMnO_4$) of $0.1N$ potassium permanganate at a rate of 25 to 35 ml per minute while stirring slowly. Let stand until the pink color disappears (about 45 seconds; if the pink color should persist because the permanganate is too strong, discard, and begin again, adding less of the $KMnO_4$ solution). Heat to 55 to 60 °C and complete the titration by adding permanganate until a faint pink color persists for 30 seconds. Add the last 0.5 to 1 ml dropwise, with particular care to allow the solution to become decolorized before the next drop is introduced.

Determine the excess of permanganate required to impart the permanent pink color to the solution. This can be done by matching the color by adding permanganate to the same volume of the specially treated dilute sulfuric acid at 55 to 60 °C. This correction usually amounts to 0.03 to 0.05 ml.

In potentiometric titrations the correction is negligible if the end point is reached slowly.

For the standardization of more dilute solutions, the same conditions are recommended except that the initial volume and size of sample are proportionally reduced.

In very accurate work the correction is best obtained iodometrically [*cf.* W. C. Bray, J. Am. Chem. Soc. **32**, 1205 (1910)] as follows: Cool the titrated solution to 25 °C, add 0.5 g of KI, 2 ml of starch solution, and titrate the liberated iodine with $0.02N$ thiosulfate. To obtain the ratio of the thiosulfate to the permanganate solution, add 1 ml of the $0.1N$ permanganate to 350 ml of the diluted sulfuric acid (5+95), stir, add 0.5 g KI, and titrate with the thiosulfate solution, adding starch just before the end point is reached.

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